dr. V. Šips

Uvod u atomsku mehaniku I

(1 - 25)

Dorezić Mirosav

TERMODINAMIKA

-zahvaljuje razvoj interesu društva

Radovi :

Carnot (1824)
Mayer (1842) } I zakon
Joule (1843) }

Kelvin (1860) } II zakon
Clausius (1851) }

Nernst (1905) III zakon

→ pokreće razvoj statist. fizike

Maxwell
početak Bernoulli (1733)
Boltzmann (1863 - 71) generalizacija
Gibbs (1902) promatra raspodjelu čest. uzimajući u obzir međudjelovanja

Planck - zrač. crnog tijela → kvanti
Bose - statistika prouzrena na fotonu } Einstein-Bose statist.
Einstein - primjena na plin
Fermi - Dirac - statist. za čije čestice vrijedi Paulijev princip

S = cijeli
S = 0, 1

S = polucijeli
S = 1/2

Planck (1900) hipoteza o kvantima energije
Bose (1924) kvanti svjetlosti
Einstein (1925) plinovi
Fermi - Dirac (1926) (Paulijev princip)

I Termodinamika
Klasična statistična fizika

II Osnovi kvantne mehanike
Kvantna statistična fizika

J. Supek : Teor. fizika i struktd. materije

Literatura:

Statistična fizika: Hrong : Statistical mechanics
Kittel : Thermal physics
Levič : Kurs teoretičeskoj fiziki I
Landau
Lifšič : Statist. fizika
Nossrev
Senkevič : Kurs statist. fizik.
Terletki : Statističeskaja fizika
Wannier : Statistical physics
Kubo : statističeskaja
statistical mechanics

Kvantna mehanika : Born : Modern Physik
Fermi : Notes on QM
Landau
Lifšic : QM.
Matthews : Introduction do Q.M.
Messiah : Q.M. I, II
Špolski : Atom. fizika

Zadaci iz Q.M. :

Gulicki : Sbornik zadač po kvant. meh.
Goldna Ruskin : - " -
Irodov : Sbornik zadač po atomnoj i jadernoj fizik.

stat. fizika : Kubo Ryogo
Landau

Elementi termodinamike

1. Definicije

Mehanički opis - zahtjeva poznavanje svih

$q_1, q_2, \ldots$ $\quad q(t)$ $\quad q(t_0)$

$p_1, p_2, \ldots$ $\quad p(t)$ $\quad p(t_0)$

u principu za sve sisteme → za velike sisteme :

Termodinamički - funkcije stanja

$V, T, P, S, U, F = A$

a) **ekstenzivni parametri:** $V, U, S, F..$

- fje. koje su proporc. količ. tvari

b) **intenzivni parametri** T, P

- fje. koje su invarijantne na količ. tvari

Kad sistem dolazi u poč. stanje, fje. stanja poprimaju iste vrijednosti ⇒ diferencijali su potpuni

$f = f(x,y)$ fja. stanja

$df = M(x,y)dx + N(x,y)dy$

Kriterij: 1. u diferencijalnom obliku $\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$

2. u integralnom obliku $\int_1^2 df = f(2) - f(1) \Rightarrow \oint df = 0$

funkcije procesa $Q, \acute{A}^{rad}$ ovise o putu

Ravnotežno stanje - veličine stanja se ne mijenjaju u vremenu

$f = \text{const}$

Termodinamički procesi - Reverzibilni $1 \to 2$ & $2 \to 1$

Ireverzibilni $1 \to 2$ $2 \not\to 1$

reverzibilni - idealizacija, u stvari prolaz kroz niz ravnotežnih stanja

2. Jba. stanja

T, V, P povezani u t-din. ravnot. stanju

$$P = f(T, V)$$

- u magnet. polju $\vec{\mathcal{H}}$ ∃ magnetizacija $\vec{M}$

$$|\vec{M}| = f(T, \mathcal{H})$$

- u elektr. polju $\vec{E}$ ∃ polarizacija $\vec{P}$

$$|\vec{P}| = f(T, E)$$

općenito: $z = f(x, y)$ $\quad dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \quad / \, dy$

$z = \text{const} \Rightarrow \quad 0 = \left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial z}{\partial y}\right)_x \quad / \cdot \left(\frac{\partial y}{\partial z}\right)_x$

$$\Rightarrow \quad \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

jer $\left(\frac{\partial z}{\partial y}\right)_x = \frac{1}{\left(\frac{\partial y}{\partial z}\right)_x}$

spec: $$\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial T}{\partial V}\right)_P \left(\frac{\partial V}{\partial P}\right)_T = -1 \qquad (1)$$

Koef. term. širenja $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$

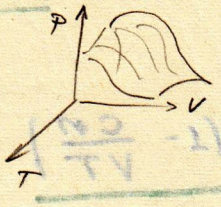
term. koef. tlaka $\beta = \frac{1}{p}\left(\frac{\partial p}{\partial T}\right)_V$

izotermna kompresibilnost $\chi = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$

$\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial p}{\partial T}\right)_V \frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \frac{1}{p} \cdot p$

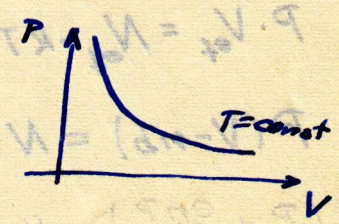
$\Rightarrow \underline{\alpha = \beta \chi \cdot p}$ (1)

- Ploha ravnotežnog stanja



Idealan plin

- udaljenost čest. znatno veća od dosega potencijala interakcije



$PV = NKT$ (N - broj čestica, K - Boltzmannova konstanta)

$\frac{K}{A}$ $\frac{N}{A} = n$

$K = 1{,}38 \cdot 10^{-16}\ erg\ st^{-1} = \frac{R}{A}$

$PV = nRT$ (n - broj molova)

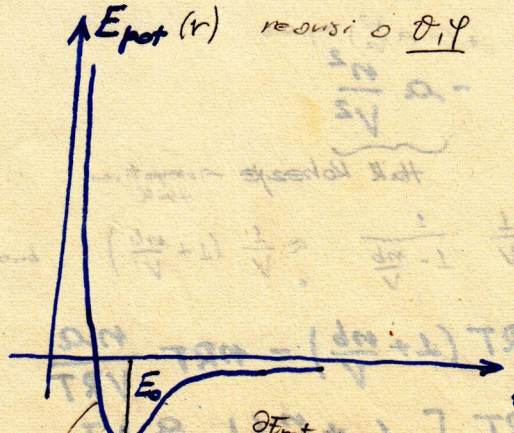
$R = A \cdot K$ $\quad A = 6{,}03 \cdot 10^{23}$

$R = 8{,}314 \cdot 10^{7}\ erg\ st^{-1} = 1{,}987 \frac{cal}{st} \approx 2\ cal/st$

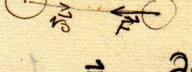
- za manje udalj. molekula exp.

$\vec{F} = -\,grad\, E_{pot}$

$grad\, E_{pot} = \vec{r_0} \frac{\partial E_{pot}}{\partial r}$



reversi o ϑ, φ



$\vec{F} = -\frac{\partial E_{pot}(r)}{\partial r} \cdot \vec{r_0}$

$\frac{\partial E_{pot}}{\partial r} > 0 \Rightarrow \vec{F} = -\left|\frac{\partial E_{pot}}{\partial r}\right| \cdot \vec{r_0}$ privlačna

$\frac{\partial E_{pot}}{\partial r} = \frac{d E_{pot}}{dr} < 0$

$\Rightarrow \vec{F} = \left|\frac{\partial E_{pot}}{dr}\right| \cdot \vec{r_0}$ odbojna

Van der Waals (1873)

- odbijanje na malim udaljenostima (najmanja pretpostavka malih tvrdih kuglica)

- efektivni volumen posude $\underline{V_{ef} = V - n \cdot b}$

korekcija ove vrsti za $V > nb$, a ne za $V \gg n \cdot b$

- privlačenje na velikim udaljenostima - broj čestica se pokazuje manjim $\underline{N_{ef}}$ - bliži pravcu uz $\frac{V}{n}$ veće - nyetiplin
- bliži pravcu uz T veće

$$\Rightarrow \underline{N_{ef} = N\left(1 - \frac{cn}{VT}\right)}$$

nema korekcije za $\frac{cn}{VT} \ll 1$

$$P \cdot V_{ef} = N_{ef} \cdot KT$$

$$P(V - nb) = N\left(1 - \frac{cn}{VT}\right) KT \quad / \left(1 + \frac{cn}{VT}\right)$$

$$(V - nb)\left(P + \frac{cnP}{VT}\right) = N\left(1 - \frac{c^2 n^2}{V^2 T^2}\right) KT$$

$\frac{c^2 n^2}{V^2 T^2} \ll 1$ $\quad P \approx \frac{nRT}{V}$

$$(V - nb)\left(P + \frac{cn}{V\cancel{T}} \cdot \frac{nR\cancel{T}}{V}\right) = NKT$$

$\underline{a = cR}$

$$\underline{\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT}$$

mjereni na stijenci $\quad$ mjereni volumen posude

$$P = \frac{nRT}{V - nb} \underbrace{- a\frac{n^2}{V^2}}_{+\left(-A\frac{n^2}{V^2}\right) \text{ zapravo}}$$

tlak kohezije → negativan tlak

$$\frac{1}{V - nb} = \frac{1}{V} \cdot \frac{1}{1 - \frac{nb}{V}} \approx \frac{1}{V}\left(1 + \frac{nb}{V}\right)$$

budući: $\frac{nb}{V} < 1 \Rightarrow \left(\frac{nb}{V}\right)^2 \ll 1$

$$\Rightarrow P \cdot V = nRT\left(1 + \frac{nb}{V}\right) - nRT \cdot \frac{na}{VRT}$$

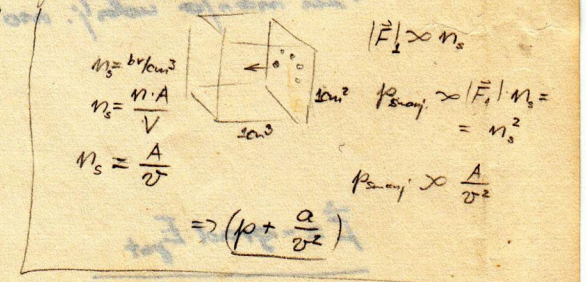
$$\underline{P \cdot V = nRT\left[1 + \frac{n}{V}\left(b - \frac{a}{RT}\right)\right]}$$ ← teorijski jasan i omogućuje

općenito: $\underline{\frac{PV}{nRT} = 1 + B(T)\left(\frac{n}{V}\right) + C(T)\left(\frac{n}{V}\right)^2 + \ldots}$ (može i $\downarrow N$, $N \to$)

virijalni razvoj

Kamerlingh-Onnes

$$(p + \frac{a}{v^2})(v - b) = RT \qquad v = \frac{V}{n}$$



3. Zakoni termodinamike

- unutar nje se ne razjašnjuje zašto?
- odgovor u statist. fizici

I zakon (Meyer, Joule)

ΔQ privedena dopl. – ne mora biti diferencijal (dodatni) neka fja $\rightarrow d'Q$

ΔU povec. unutr. energ.

ΔA rad koji izvrši sistem (+)

$$\Delta Q = \Delta U + \Delta A$$

$$\underline{d'Q = dU + d'A} \quad (1)$$

→ zbog fja. procesa, one stanja

$$dU = d'Q - d'A$$

→ fja stanja

$$\Rightarrow \underline{\oint dU = 0}$$

Toplinski kapacitet

$$C = \lim_{\Delta T \to 0} \frac{\Delta Q}{\Delta T} = \frac{dQ}{dT} \qquad c = \frac{C}{m} \quad \text{spec. toplina}$$

- ako sistem vrši mehanički rad $d'A = p\,dV$

$$I \rightarrow \quad d'Q = dU + p\,dV \qquad f(p,V,T) = 0 \qquad U = U(V,T)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

$$\Rightarrow \left(\frac{\partial U}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V \cdot \left(\frac{\partial T}{\partial T}\right)_p + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p$$

"1"

$$\Rightarrow \underline{d'Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right] dV} \quad (*)$$

$V = \text{const.} \quad C = \frac{d'Q}{dT} \Rightarrow \quad (d'Q)_V = \left(\frac{\partial U}{\partial T}\right)_V dT$

$$\underline{C_V = \left(\frac{\partial U}{\partial T}\right)_V}$$

entalpija

$P = \text{const} \Rightarrow (d'Q)_p = d(\underbrace{U + pV}_{H}) \Rightarrow \underline{C_p = \left(\frac{\partial H}{\partial T}\right)_p} \qquad \underline{H = U + pV}$

$$(d'Q)_p = \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right] dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

$$C_p = \left[p + \left(\frac{\partial U}{\partial V}\right)_T\right] \cdot \left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial U}{\partial T}\right)_V = \left(\frac{\partial U}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_p + \left(\frac{\partial U}{\partial T}\right)_V + p\left(\frac{\partial V}{\partial T}\right)_p$$

$$C_p = \left(\frac{\partial U}{\partial T}\right)_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\cdot\left(\frac{\partial V}{\partial T}\right)_P \qquad C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

$$\Rightarrow \quad C_p - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\cdot\left(\frac{\partial V}{\partial T}\right)_P \qquad = \left(\frac{\partial U}{\partial T}\right)_P \cdot \left(\frac{\partial P}{\partial V}\right)_T$$

$$= T\cdot\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \quad (2)$$

$$= -T\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T > 0$$

$\downarrow 0 \qquad \uparrow 0$

$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$
$dU = TdS - pdV$
$TdS = C_V dT + T\left(\frac{\partial p}{\partial T}\right)_V dV$
$\Rightarrow$ jba. energije $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$

Ilustracija: - idealni plin

$$PV = nRT \quad \Rightarrow \left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P} \quad \& \quad \left(\frac{\partial U}{\partial V}\right)_T = 0 \quad \text{iz def. idealnog plina}$$

$$\Rightarrow \quad C_p - C_V = P\cdot\frac{nR}{P} = nR \quad \Rightarrow \underline{C_p > C_V}$$

budući postoji dopline ide na vršenje rada kod C_p, kad se plin rasteže

(1) $Q(T,V)$

$$(*) \Rightarrow \quad d'Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]dV$$

$$\left\{\frac{\partial}{\partial T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\right\}_V - \left\{\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right\}_T = \left(\frac{\partial P}{\partial T}\right)_V \neq 0$$

i za idealan plin

$\Rightarrow d'Q$ nije totalni diferencijal

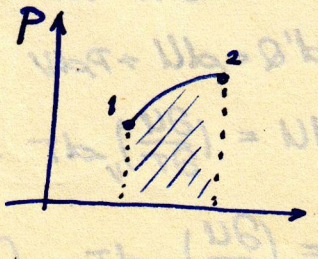
ako U - fja. stanja $\Rightarrow \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_V = \left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right)_T$

ili: $\left(\frac{\partial^2 U}{\partial V \partial T}\right)_{T,V} = \left(\frac{\partial^2 U}{\partial T \partial V}\right)_{V,T}$

$$\Rightarrow \quad \underline{\oint d'Q \neq 0}$$

$$\oint d'Q = \underbrace{\oint dU}_{0} + \oint d'A = \oint d'A \quad \Rightarrow \underline{\oint d'A \neq 0}$$

$$A_{12} = \int_1^2 P\,dV$$



$$d'A = P\,dV$$

$$\underline{d'A = \sum_i R_i\, dr_i} \qquad \underline{R_i} \text{ - intenzivna veličina (poopćena sila)}$$

$\underline{dr_i}$ - diferencijal ekstenzivne veličine (poopćena koordinata)

$E_{pot} = -\vec{\mu}\cdot\vec{H} = -\mu_0 \mu_H |\vec{H}|$

$E = \int_{\text{podintl. volumen}} E_{pot}\, dV = -|\vec{H}| \int \mu_0 \mu_H\, dV = -\mu_0 |\vec{M}||\vec{H}|$

$\Rightarrow dE_{pm} = -\mu_0 H \cdot dM \Rightarrow dW_v = \mu_0 H dM$

rad po jedinici volumena

$W_v = \mu H^2 = \mu_0 H (1+\chi_m) H = \mu_0 H^2 + \mu_0 H \cdot M$

$\Rightarrow dW_v = \mu_0 H \cdot dM$ $\quad dM>0 \Rightarrow dW_v > 0$

$W_v > 0$ uloženi rad — uloženi rad raste

$\Rightarrow dM>0 \Rightarrow dW_v>0$ $\quad A' = -W_v$ $\quad W_v>0$ uloženi rad sist. $A'<0$ uloš. rad sist $|W_v| = |A'|$

$\Rightarrow \underline{dA' = -\mu_0 H dM}$

Ilustracija

1. Rad utrošen za magnetizaciju M

($\mu_0 = 1$ u cgs sustavu jedinica)

$$d'A = -H\,dM$$

$dM>0$ na račun polja H

$d'A<0$ (sistem dobiva rad)

2. polarizacija P $\quad d'A = -E\,dP$

II zakon

- preko Clausiusove nejednakosti (analizom Carnot-ovog procesa)

$$\oint \frac{d'Q}{T} \leq 0$$ ireverz. / reverz. (3)

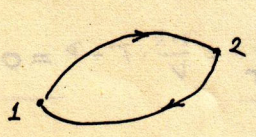
reverz. $\oint_R \frac{d'Q}{T} = 0 \Rightarrow \underline{dS = \frac{d'Q}{T}}$ (4)

$$S(B) - S(A) = \int_A^B dS = \int_A^B \frac{d'Q}{T}$$

entropija def. za reverz. procese do na aditivnu konst.

P - referentno stanje $\quad \underline{S(A) = \int_P^A \frac{d'Q}{T}}$ (5)

Kružni proces



$1 \to 2$ nespecificirano

$2 \to 1$ reverzibilan

$\Big\} \Rightarrow$ ○ ireverz. dij. operacija

$$\int_1^2 \frac{d'Q}{T} + \int_{2(r)}^1 \frac{d'Q}{T} \leq 0$$

$\frac{M(T,V)}{T} dT + \frac{N(T,V)}{T} dV$

$$\Rightarrow S(2) - S(1) = \int_{1(r)}^2 \frac{d'Q}{T} = dS' \geq \int_1^2 \frac{d'Q}{T}$$

u limesu $\lim_{2\to 1} S(2) - S(1) = dS$

$\lim_{2\to 1} \int_1^2 \frac{d'Q}{T} = \frac{d'Q}{T}$

$$\Rightarrow \underline{dS \geq \frac{d'Q}{T}}$$ ireverz. / reverz. (6) $\Leftrightarrow$ (3)

Sistem term. izoliran (zatvoren)

- adijabatski proces $\Rightarrow d'Q = 0 \Rightarrow \underline{dS \geq 0}$

entropija izoliranog sistema može se samo povećati

I z.t.d. vrijedi egzaktno

II z.t.d. vrijedi u prosjeku → ∃ fluktuacije (odstupanja) od II zakona (statist. fizika)

∃ prijelaz $S_1 \to S_m > S_1$ $\quad S_m \approx S_1$

toplinska smrt (max. S svemira)

- ∃ podsistemi svemira u kojima se S bilo smanjuje, bilo povećava ⇒

⇒ u srednjem nepromijenjeno

- 12 Paića ⇒ S nekog podsistema može rasti ili padati, ali se S cijelog svemira može samo povećati

$U = U(T,V)$ $\quad dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$

$$dS = \frac{d'Q}{T} = \frac{dU + P\,dV}{T} = \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT + \frac{1}{T}\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV$$

$T = T(p,V)$

II z.d.d. za revers. proces dS tod. dif. ⇒

$$\left\{\frac{\partial}{\partial V}\left[\frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V\right]\right\}_T = \left\{\frac{\partial}{\partial T}\left[\frac{1}{T}\left(P + \left(\frac{\partial U}{\partial V}\right)_T\right)\right]\right\}_V$$

$$-\frac{1}{T^2}\cdot\left(\frac{\partial T}{\partial V}\right)_T + \frac{1}{T}\left(\frac{\partial^2 U}{\partial T \partial V}\right)_{V,T} = -\frac{1}{T^2}\left(\frac{\partial T}{\partial T}\right)_V \cdot \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] + \frac{1}{T}\left(\frac{\partial P}{\partial T}\right)_V + \frac{1}{T}\left(\frac{\partial^2 U}{\partial V \partial T}\right)_{T,V}$$

($\left(\frac{\partial T}{\partial V}\right)_T = 0$, $\left(\frac{\partial T}{\partial T}\right)_V = 1$, isto U-fja stanja)

$$\boxed{T\left(\frac{\partial P}{\partial T}\right)_V = P + \left(\frac{\partial U}{\partial V}\right)_T}$$ jed. energije (7)

(2) & (7) ⇒ $$\boxed{C_p - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_p}$$

idealan plin: $PV = nRT \Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$ ⇒ $\left(\frac{\partial U}{\partial V}\right)_T = \frac{nR}{V}\cdot T - P = 0$

→ U analogiji s izvodom (7) jer vrijedi I $dU = d'Q - d'A$ II rev. $dS = \frac{d'Q}{T}$

Magnetski sistem $\quad d'A = -\mathcal{H}\,dM \quad U = U(T,M)$

$\vec{B} = \mu\vec{H} = \mu_0(\vec{H} + \vec{M}_V)$ ⇒

$$\boxed{-T\left(\frac{\partial \mathcal{H}}{\partial T}\right)_M = -\mathcal{H} + \left(\frac{\partial U}{\partial M}\right)_T}$$

$\vec{M}_V$ - magnetizacija po jedinici volumena dveri

$\vec{M}_V = \frac{d\vec{m}}{dV}$ $\quad \vec{m} = \int_V \vec{M}_V dV$

$\frac{dW}{dV} = W_V = \mu H^2$ spec rad

$$C_{\mathcal{H}} - C_M = \left[\left(\frac{\partial U}{\partial M}\right)_T - \mathcal{H}\right]\left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}}$$

$$\boxed{C_{\mathcal{H}} - C_M = -T\left(\frac{\partial \mathcal{H}}{\partial T}\right)_M \left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}}}$$

p, V const

$P \ldots -\mathcal{H}$

$dM \ldots dV$

$d'Q = dU - \mathcal{H}\,dM = \left(\frac{\partial U}{\partial T}\right)_M dT + \left(\frac{\partial U}{\partial M}\right)_T dM - \mathcal{H}\,dM$

$M = \text{const} \quad C_M = \left(\frac{d'Q}{dT}\right)_M = \left(\frac{\partial U}{\partial T}\right)_M$

$\mathcal{H} = \text{const} \quad C_{\mathcal{H}} = \left(\frac{\partial (U - \mathcal{H}M)}{\partial T}\right)_{\mathcal{H}} =$

$= \left(\frac{\partial U}{\partial T}\right)_M + \left(\frac{\partial U}{\partial M}\right)_T \left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}} - \mathcal{H}\left(\frac{\partial M}{\partial T}\right)_{\mathcal{H}}$

$M = \chi \mathcal{H}$ (χ ... susceptibilnost)

dijamagneti: $\chi < 0$ & $\frac{\partial M}{\partial T} = 0$ (per temp. malo utječe na strukturu i stanje $\vec{e}$) $\Rightarrow C_{\mathcal{H}} = C_M$

paramagneti: $\chi > 0$ & u odred. T intervalu Curie-ev zakon

$$M = a \frac{\mathcal{H}}{T}$$ idealni paramagneti

$$\left(\frac{\partial U}{\partial M}\right)_T = \mathcal{H} - T\frac{M}{a} = \mathcal{H} - \mathcal{H} = 0$$

$$\Rightarrow \left(\frac{\partial U}{\partial M}\right)_T = 0$$

unut. energija ne ovisi o magnetizaciji već samo o temperaturi

jasno i per magnetizacija ovisi o T

$+T\frac{M}{a}\cdot\left(-\frac{a}{T^2}\right)\mathcal{H}$

$$\Rightarrow C_{\mathcal{H}} - C_M = \frac{\mathcal{H}\cdot M}{T} > 0$$

$C_{\mathcal{H}} > C_M$ budući jedan dio topline ide na vršenje rada kad $C_{\mathcal{H}}$ kad se tvar magnetizira (?)

Dielektr. sistem $d'A = -E\,dP$

P .... $-E$

dV .... dP $\quad U(T, P)$

$$C_E - C_P = -T\left(\frac{\partial E}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_E$$

jba. idealnog dielektrika:

Curiev zakon: $b = \frac{Nd^2}{3K}$ (a=0)

$$P = b\frac{E}{T}$$

$$\left(\frac{\partial U}{\partial P}\right)_T = E + T\left(\frac{\partial E}{\partial T}\right)_P = E + T\cdot\frac{P}{b} = 0$$ (E)

$$\Rightarrow \left(\frac{\partial U}{\partial P}\right)_T = 0$$

unut. energija ne ovisi o polarizaciji već samo o temperaturi

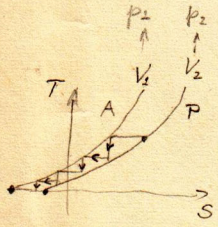
$-T\cdot\left(\frac{P}{b}\right)\left(-\frac{b}{T^2}\right)E$

$$C_E - C_P = \frac{E}{T}\cdot P$$ (E ... ekstenzivna veličina)

$\rightarrow$ analogija $C_p - C_V = R = \frac{pV}{T}$ - ekstenz. veliče.

III zakon Nernst (1905) $\quad \lim_{T\to 0} S = 0$

Entropija sistema ne može pasti ispod neke vrijednosti.
Za homogena tijela da min. vrijednost je ili nula ili beznačajno mala prema entropiji na običnim temperaturama.



$$S(A) = \int_P^A \frac{d'Q}{T} = \int_P^A \frac{d'Q}{T}\frac{dT}{dT}$$

$$C(T) = \frac{d'Q}{dT}$$ topl. kapacitet

$$S(A) = \int_P^A C(T)\frac{dT}{T}$$

Kad bi $\int_{T=0}\left[S(A) - S(P)\right] \neq 0$ tada bi se kon. brojem procesa mogli postići $T=0$

$\Downarrow$

ako $S(P) = 0$ $\Rightarrow$ $S(A) \neq 0$

za $C(T) = \text{const}$ ($[A,B]$ dovoljno mali golf je to zadovoljio)

$\Rightarrow S \sim \ln T \Rightarrow S(0°K) \to -\infty$

Nernst $\Rightarrow$ topl. kapacitet za $T\to 0$ mora iščezavati

tj. $\lim_{T\to 0} C(T) = 0$ (8) Kamen spoticanja za klas. odnosno kvant. fiziku

Sistemi u termičkom kontaktu

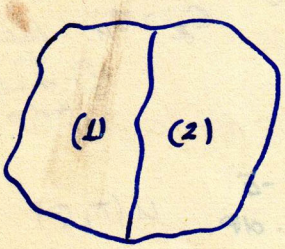
Pitanje ravnoteže izoliran. sistema → podsistema u term. kontaktu

Stanje t-din. ravnoteže ⇒ revers. procesi

t-din. procesi $\xrightarrow{\text{def.}}$ revers. procesi $\Rightarrow dS = \frac{d'Q}{T}$

za adijabatske procese (nema izmjene topl. sa okol.) $d'Q = 0 \Rightarrow dS = 0$

$dS = 0$ S aditivna extenz. veličina $\Rightarrow dS = dS_1 + dS_2$



$V = V_1 + V_2 = \text{const} \Rightarrow dV_1 = -dV_2$

$U = U_1 + U_2 = \text{const} \Rightarrow dU_1 = -dU_2$

ext	V_1	V_2
	U_1	U_2
	S_1	S_2
int	T_1	T_2
	P_1	P_2

$$dS_1 = \frac{d'Q_1}{T_1} = \frac{1}{T_1} dU_1 + \frac{P_1}{T_1} dV_1$$

$$dS_2 = \frac{d'Q_2}{T_2} = \frac{1}{T_2} dU_2 + \frac{P_2}{T_2} dV_2 \quad (-dU_1) \quad (-dV_1)$$

$\Rightarrow$

$$dS = dS_1 + dS_2 = \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) dV_1$$

$dS = 0 \xrightarrow{U, V \text{ nezav. varijable}} T_1 = T_2 \quad P_1 = P_2 \quad (*)$

⇒ da bi dva podsistema (dovedena) u term. kontaktu bili u stanju t.-din. ravnoteže mora biti (*)

t-din. ravnoteža u smislu da nema promjene S čitavog sistema $\Rightarrow dS = 0$

naime $dS = 0$ i $d'Q = 0$ (oklop adijab.) & $dS \geq \frac{d'Q}{T}$ REV. ⇒ REV. proces ⇒ t.-din. ravnoteža

Prijelaz u t-din. ravnotežu ⇒ iREV. procesi

irev. proces $dS > \frac{d'Q}{T}$

sistem u adijab. oklopu $d'Q = 0$

$\Rightarrow dS > 0$

$$\Rightarrow \left(\frac{1}{T_1} - \frac{1}{T_2}\right) dU_1 + \left(\frac{P_1}{T_1} - \frac{P_2}{T_2}\right) dV_1 > 0$$

U, V nezav. varijable; + sumand > 0

za $T_1 > T_2 \Rightarrow dU_1 < 0 \Rightarrow dU_2 > 0$ U_1 smanjuje, U_2 ↑

Uvjeti t-din. ravnoteže

REV. $dS = \frac{d'Q}{T}$

IREV. $dS > \frac{d'Q}{T}$ ne $\exists$ proces: $dS < \frac{d'Q}{T}$

$d'Q = dU + d'A$ $\quad d'A = \sum_i R_i \, dr_i$ (poopćena sila - int. vel. / poopć. koord - ext. vel.)

za $\forall$ proces

$$\Rightarrow \quad T\,dS \geq dU + \sum_i R_i \, dr_i \qquad (1)$$ osnovna t-din. relacija

(1) $\Rightarrow$ 4 različ. t-din. procesa

a) tokom procesa $S, r_i, \forall i = \text{const}$ $\quad dS = 0 \quad dr_i = 0 \ \forall i$

$\rightarrow$ pri/tokom prijelaza u t-din. ravnotežu $\quad dU \leq 0$

b) $S, R_i = \text{const} \quad dS = 0$

$$d\left(U + \sum_i R_i r_i\right) \leq 0$$

entalpija $H = U + \sum_i R_i r_i$ $\Rightarrow \quad dH \leq 0$

c) $T, r_i, \forall i = \text{const} \quad dr_i = 0$

$$d(U - TS) \leq 0$$

Helmholtzova fja A

slobodna energija $F = U - TS$ $\Rightarrow \quad dF \leq 0$

d) $T, R_i, \forall i = \text{const}$

$$d\left(U + \sum_i R_i r_i - TS\right) \leq 0$$

slobodna entalpija (Gibbs-ov potencijal) $G = U + \sum_i R_i r_i - TS$ $\Rightarrow \quad dG \leq 0$

$G = +/- TS$

Maxwell-ove relacije - za sistem u stanju t-din. ravnoteže

ograničenje $d'A = pdV \Rightarrow dS = \frac{1}{T}dU + \frac{p}{T}dV$

$\Rightarrow \frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_V \quad \frac{p}{T} = \left(\frac{\partial S}{\partial V}\right)_U$, $F_x = -\frac{\partial U}{\partial x}$

U	$\Rightarrow dU = TdS - pdV$	$\Rightarrow T = \left(\frac{\partial U}{\partial S}\right)_V$	$p = -\left(\frac{\partial U}{\partial V}\right)_S$	
slob. energija $F = U - TS$	slob. $\Rightarrow dF = -pdV - SdT$	$\Rightarrow p = -\left(\frac{\partial F}{\partial V}\right)_T$	$S = -\left(\frac{\partial F}{\partial T}\right)_V$	
$H = U + pV$	$\Rightarrow dH = TdS + Vdp$	$\Rightarrow T = \left(\frac{\partial H}{\partial S}\right)_p$	$V = \left(\frac{\partial H}{\partial p}\right)_S$	
slob. entalpija $G = H - TS$	$\Rightarrow dG = -SdT + Vdp$	$\Rightarrow S = -\left(\frac{\partial G}{\partial T}\right)_p$	$V = \left(\frac{\partial G}{\partial p}\right)_T$	

$$T = \left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right)_p$$

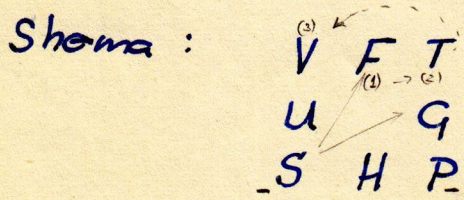
$$\Rightarrow \quad p = -\left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial U}{\partial V}\right)_S$$

T, p, S, V preko U, F, H, G (extenz. veliče)

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = -\left(\frac{\partial G}{\partial T}\right)_p$$

$$V = \left(\frac{\partial H}{\partial p}\right)_S = \left(\frac{\partial G}{\partial p}\right)_T$$

Shema:



sredina kvadrata → naspramni mu & strana

$$T = \left(\frac{\partial H}{\partial S}\right)_p \qquad p = -\left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial U}{\partial V}\right)_S$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V(3)}^{(1)} = -\left(\frac{\partial G}{\partial T}\right)_p$$

(2)

Gibbs-Helmholtz-ova jba.

$$F = U - TS \quad (S = -\left(\frac{\partial F}{\partial T}\right)_V) \quad = U + T\left(\frac{\partial F}{\partial T}\right)_V \quad \Rightarrow U = F - T\left(\frac{\partial F}{\partial T}\right)_V$$

$$G = H - TS \quad (S = -\left(\frac{\partial G}{\partial T}\right)_P) \quad = H + T\left(\frac{\partial G}{\partial T}\right)_P \quad \Rightarrow H = G - T\left(\frac{\partial G}{\partial T}\right)_P$$

inverzne relacije integriranjem →

$$-\frac{U}{T^2} = -\frac{F}{T^2} + \frac{1}{T}\left(\frac{\partial F}{\partial T}\right)_V = \left(\frac{\partial}{\partial T}\frac{F}{T}\right)_V$$

$$-\frac{H}{T^2} = -\frac{G}{T^2} + \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_P = \left(\frac{\partial}{\partial T}\frac{G}{T}\right)_P$$

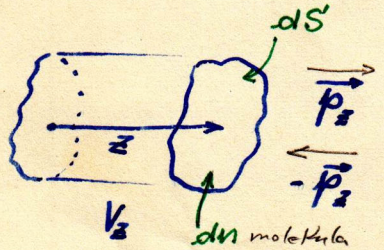
$$\Rightarrow \quad F = -T\left[\int \frac{U}{T^2}\,dT + f(V)\right]$$

$$G = -T\left[\int \frac{H}{T^2}\,dT + g(P)\right]$$

Pritisak idealnog plina

jednoatomni & zanemarive sile

$$U = \sum_{i=1}^{N} \frac{m v_i^2}{2}$$



$$\Delta \vec{p}_z = 2\vec{p}_z$$

zbog izotropnosti od N molek. u V

eff. $\frac{N}{2}$ molekula putuje u $+z$ smjeru

$\Rightarrow$ eff. gustoća $\frac{N}{2V}$

$$\Rightarrow \quad \overline{dn} = \frac{N}{2V} \cdot \overline{V_z}\,dt\,dS$$ → prosječno toliko molekula udari u dS unutar dt

prosječni impuls predan dS u dt

$$\overline{dp_z} = \overline{dn} \cdot \overline{\Delta p_z} = \frac{N}{2V}\,\overline{V_z} \cdot 2\overline{p_z}\,dt\,dS$$

prosječna sila na dS

$$\overline{dF_z} = \frac{\overline{dp_z}}{dt} = \frac{N}{V}\,\overline{p_z \cdot V_z}\,dS$$

↓ nema potrebe još tu

!!! napomena: nevrijedi $\overline{V_z \cdot p_z} = \overline{V_z} \cdot \overline{p_z}$ jer su V_z & p_z međusobno zavisne veličine

$p \cdot V$
$\parallel$
$mv \cdot v$
$m\vec{v} \cdot \vec{v} = \vec{p} \cdot \vec{v} =$

$$pV = p_x V_x + p_y V_y + p_z \cdot V_z$$

$$\overline{pV} = S\overline{p_x V_x} \qquad \overline{p_x V_x} = \overline{p_y V_y} = \overline{p_z \cdot V_z} \quad \Rightarrow \quad \overline{p_z \cdot V_z} = \frac{1}{3}\overline{p \cdot V}$$

$$\Rightarrow \quad p = \frac{\overline{dF_z}}{dS} = \frac{N}{3V}\overline{pV}$$

$$E = \frac{mv^2}{2} = \frac{p \cdot v}{2} \quad \Rightarrow \overline{pV} = 2\bar{E}$$

$$\Rightarrow \quad \underline{\underline{p = \frac{2N\bar{E}}{3V}}}$$

Bernoulli, 1738

$$U = \sum_{i=1}^{N} E_i \quad \Rightarrow \bar{U} = \sum_{i=1}^{N} \bar{E}_i = N\bar{E}$$

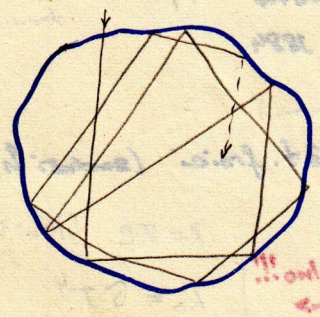
$$U = \bar{U} = N\bar{E}$$

$$\underline{\underline{PV = \frac{2}{3}U}} \quad \text{za idealan plin}$$

$$P \cdot V = N \cdot K \cdot T \quad \Rightarrow \quad NK\bar{T} = \frac{2}{3}N\bar{E}$$

$$\Rightarrow \quad \underline{\underline{\bar{E} = \frac{3}{2}KT}}$$

Zračenje crnog tijela



- posuda volumena V
- u stanju t-plin. ravnoteže temp. T

el. m. zračenje

1° el. m. valovi

2° skup ekvivalentnih (quasi) čestica - fotona (fotonski plin)

2° ⇒ relativist. fizika ⇒ $E = c\sqrt{p^2 + m_0^2 c^2}$

a) $p = 0 \rightarrow E = m_0 c^2$

$E = m(v)c^2 \quad m(v) = \frac{m_0}{\sqrt{1 - (\frac{v}{c})^2}}$

b) $m_0 = 0 \rightarrow \underline{E = c \cdot p}$

quasi-čestice

1° ⇒ de Broglie ⇒ $E = h\nu$, $E = c \cdot p$, $c = \lambda \cdot \nu$ ⇒ $h\nu = \lambda\nu p$ ⇒ $\underline{p = \frac{h}{\lambda}}$

2° za fotone $\overline{pV} = pc = \overline{E}$ a ne kao inače $\overline{E} = \frac{m\overline{v^2}}{2} = \frac{1}{2}\overline{pV}$

$\underline{P = \frac{N}{3V}\overline{pV} = \frac{N\overline{E}}{3V}} \qquad U = N\overline{E}$

(*) $\underline{P = \frac{U}{3V}}$ $\qquad \underline{U(T,V) = V \cdot u(T)}$ ← gustoća energije

⇒ $\underline{P = \frac{u}{3}}$

!!! bitna separacija varijabli $f(V) \cdot u(T)$ ozbiljno da je ovdje moguće pisati $f(V) = V$!!!

II z.t.d $\oint dS = 0$ ZAREV. $= dS$ tot. dif ⇒ $T\left(\frac{\partial P}{\partial T}\right)_V = P + \left(\frac{\partial U}{\partial V}\right)_T$

(*) ⇒ $T\left(\frac{\partial P}{\partial T}\right)_V = P + \left(\frac{\partial U}{\partial V}\right)_T$

$\left(\frac{\partial U(T,V)}{\partial V}\right)_T = u(T)$

$\left(\frac{\partial P}{\partial T}\right)_V = \frac{1}{3}\left(\frac{\partial u(T)}{\partial T}\right)_V = \frac{1}{3}\frac{du}{dT}$

$T\frac{1}{3}\frac{du(T)}{dT} = \frac{u(T)}{3} + u(T)$

⇒ $\frac{4}{3}u(T) = \frac{1}{3}T\frac{du(T)}{dT}$

$\int 4\frac{dT}{T} = \int \frac{du}{u}$

$\Rightarrow \quad 4 \ln T + \ln a = \ln u$

→ unut. energija jedinice volumena fotonskog plina ⟶ $u = aT^4$ **Stefan 1874** **Boltzman 1884** - promatrao zračenje šupljine termometra

→ $P = \sigma T^4$ energija izlazna - ukupno i apsorbirana (iz jedinice volumena, u jedinicu volumena)

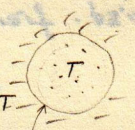
- integraciona konst. a nepoznata u klas. statist. fizici (sadrži $\hbar$)

$R = \pi \cdot B \quad [W m^{-2}] \quad B = W m^{-2} sr^{-1}$

originalno!!! →

$R_0 = \sigma T^4$

T - temp tijela i fotonskog plina



$E_{emit.} = S \cdot \sigma T^4 \cdot t \quad \Leftrightarrow$

$\Leftrightarrow$ emisija N fotona

$U = N\bar{E} = VaT^4$

V - volumen unutrašnjosti šupljine

$U = E_{emit.}$ gdje je t vrijeme potrebno za emisiju N fotona (u volumenu V) pritom se uspostavi termodinamička ravnoteža između fotonskog plina i crnog tijela ↳

t. emisija fotona jednaka apsorbiranje, dakle kad zbog $N \neq$ dovoljno poraste P fotonskog plina

⇒ Konzekvencije:

$$P = \frac{u}{3} = \frac{1}{3} a T^4$$

$$U = V \cdot u = V a T^4$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = 4aVT^3$$

$$S = \int_0^T C_V \frac{dT}{T} = \int_0^T 4aVT^2 dT = 4aV \int_0^T T^2 dT = \frac{4}{3} aVT^3 \qquad \text{for } S(0) = 0$$

$$F = -\frac{1}{3} U \qquad U - TS = VaT^4 - \frac{4}{3} aVT^4 = -\frac{1}{3} aVT^4$$

$$H = \frac{4}{3} U \qquad U + PV = aVT^4 + \frac{1}{3} aVT^4 = \frac{4}{3} aVT^4$$

$$G = 0 \qquad H - TS = \frac{4}{3} U - \frac{4}{3} aVT^4 = 0$$

(br. fotona nije očuvan) (*)

!!!

!!! I z.t.d. $dU = -d'Q - d'A = TdS - PdV$ za REV.

II z.t.d. $\oint \frac{d'Q}{T} = 0 \Rightarrow dS = \frac{d'Q}{T}$ tot. dif. za REV. $\Rightarrow dS = \frac{1}{T} dU + \frac{P}{T} dV \Rightarrow (7)$

? → sudite privatni. dase u fotonskom plinu odvijaju samo REV. procesi. i da vrijedi II z.t.d.

Statistička fizika

Martinis: Most ieuacten t-dinamike i molekularno atomske slike

Hlić: Statisd - t-dinam. → računanje t-din. fja preko particione fje.

Pretp. (treba znati tip Hamiltonijana) → Q.M.
- fenomenološka t-din.

Pretp: Poznate jbe. stanja

- Kl. meh. → do problema više tijela

$\Delta x \cdot \Delta p_x \approx h$ $\quad E, E+dE$

velik broj čestica → $g(E)$ f-ja raspodjele
obuhvaća
⊃ fiz. mnoštva čestica

1° Klasična

2° Kvantna - neki rezultati se slažu s rezultatima Klas.

Granice Klas. stat. fizike

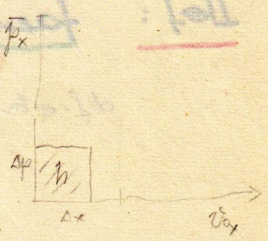
$$\left.\begin{aligned}\Delta x \cdot \Delta p_x &\gtrsim h\\ \Delta y \cdot \Delta p_y &\gtrsim h\\ \Delta z \cdot \Delta p_z &\gtrsim h\end{aligned}\right\} \Rightarrow \Delta x \Delta y \Delta z \, \Delta p_x \Delta p_y \Delta p_z \gtrsim h^3$$

$$\bar{E} = \frac{3}{2}KT = \frac{\bar{p}^2}{2m} \qquad \bar{p}^2 = 3KTm \rightarrow \sqrt{\bar{p}^2} \approx \bar{p}$$

$$\Rightarrow \bar{p} \approx \sqrt{mKT} \qquad v_0 = \frac{V}{N}$$ volumen na 1 čest.

$\Delta x \Delta y \Delta z$

$$\Rightarrow v_0 \bar{p}^3 \approx \frac{V}{N}(mKT)^{3/2}$$



beznačajna uloga Kvant. efekata za:

$$\frac{\Delta x \Delta y \Delta z \, \Delta p_x \Delta p_y \Delta p_z}{v_0 \bar{p}^3} \ll 1 \qquad \left(\approx h^3\right) \qquad \frac{v_0 \bar{p}^3}{h^3} \gg 1$$

$$\frac{V(mKT)^{3/2}}{h^3 \cdot N} \gg 1$$

uvjet primjenjivosti Klas. statističke fizike

čestice
za $V \gg 1$ $m \gg 1$ $T \gg 1$ $\Leftrightarrow$ $h \to 0$

$6{,}02 \cdot 10^{23} \,/\, 22{,}400\ cm^3 = \frac{6}{2} \cdot 10^{23-4} = 3 \cdot 10^{19}$

$g\,cm/s^2 \cdot cm$
$g\,cm^2\,s^{-2}$

Primer: Plin H_2 $T = 300K$ $\frac{N}{V} = 2{,}7 \cdot 10^{19}\ cm^{-3}$

$\Rightarrow \frac{V(mKT)^{3/2}}{N h^3} = 6 \cdot 10^3 \gg 1$; klas. je primenjiva

$= \frac{27 \cdot 10^{-76}\ g^3 cm^6 s^{-3}}{300 \cdot 10^{-81} (g\,cm^2 s^{-2})^3 \cdot s^3} = 27 \cdot 10^2 = 2{,}7 \cdot 10^3$

proverimo!!!

$\frac{1}{6} \cdot 10^{-23}\ g$

$\frac{1}{2{,}7 \cdot 10^{19}\ cm^{-3}} \left(1{,}38 \cdot 10^{-16}\ erg\,st \cdot 3 \cdot 10^2\ st\right)^{3/2} cm^{+3}$

$6{,}62 \cdot 10^{-27}\ erg\,s$

$= \frac{1}{2{,}7 \cdot 10^{19}} \cdot \left(0{,}69 \cdot 10^{-37}\ g^2 cm^2 s^{-2}\right)^{3/2} cm^{+3}$

$(6{,}62 \cdot 10^{-27})^3\ erg^3 s^3$

$= \frac{1}{2{,}7 \cdot 10^{19}} \cdot (\sqrt{6{,}9})^3\ 10^{-3 \cdot 19}\ g^3 cm^6 s^{-3}$

$300 \cdot 10^{-81}\ erg^3 s^3$

Liouville-ov teorem

$f(q, p, t)$

Sistem čestica Hamilt. fje. $H = f(q, p) = \sum_{k=1}^{s} p_k \dot{q}_k - L = \sum_{k=1}^{s} \left(\frac{\partial L}{\partial \dot{q}_k} \dot{q}_k - L\right)$

h=0 uvjeta s- st. slobode

$q \dots q_1, q_2, \dots q_s \quad s = 3N$

$p \dots p_1, p_2, \dots p_s$

$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j}\right) - \frac{\partial L}{\partial q_j} = 0 \quad h = 0 \quad j = 1, \dots r$

$h = r - s$

$\Rightarrow r = s$

$p_j = \frac{\partial L}{\partial \dot{q}_j} \quad \dot{p}_j = \frac{\partial L}{\partial q_j}$

- Kanonske jbe: $p_k = p_k(q_1^0 \dots q_s^0, p_1^0 \dots p_s^0, t)$

$q_k = q_k(q_1^0 \dots q_s^0, p_1^0 \dots p_s^0, t) \quad k = 1, \dots s$

$\frac{\partial H}{\partial p_j} = \dot{q}_j \quad - \frac{\partial H}{\partial q_j} = \dot{p}_j \quad j = 1, \dots s$

$\frac{dH}{dt} = \frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t}$

Klasične teorijske mehanike (*) $\frac{dq_k}{dt} = \frac{\partial H}{\partial p_k} \quad \frac{dp_k}{dt} = -\frac{\partial H}{\partial q_k} \quad k = 1, \dots s$

ako L ne ovisi eksplicitno o vremenu $\Rightarrow$ H vrem. konst.

& Konz. sile $\Rightarrow L = T - U$

$H = T + U = E$

H - zavisi od dinam. detalja : tip interakcije među česticama

postojanje veza

Def: **fazni prostor** ϕ (konstrukcija omogućena simetrijom) $2S = 6N$ dimenzije

$S = KN$ br. st. slob. molekula

dif. element $d\phi = dq_1 dq_2 \dots dq_s\, dp_1 \dots dp_s$ dimenzije

fazni prostor molekule - μ $2s$ - dimenzije s - broj st. slobode molekule

$\rightarrow$ gibanjem reprezentativna točka **fazne točke** nastaje **fazna trajektorija**

$(q^{(t)}, p^{(t)}) \equiv (q_1(t), \dots q_s(t), p_1(t), \dots p_s(t))$ parametarski (preko t) zadana krivulja

Klas. mech. & Konz. sile $\Rightarrow H(q, p) = E$ **fazna hiperploha** na kojoj se nalaze sva reprez. stanja sist. molekula

pa i sve fazne trajektorije (za $\neq$ poč uvjete)

N - molekula $\quad h = 1, \dots N$

$q(q_1, \dots q_s)$ $\qquad k = 1, \dots s$

$p(p_1, \dots p_s)$ $\qquad s = 3N$

h-ta molekula $\quad m_h \quad q_h = x_h \quad q_{h+1} = y_h \quad q_{h+2} = z_h$

$$p_h = m_h \dot{x}_h \quad p_{h+1} = m_h \dot{y}_h \quad p_{h+2} = m_h \dot{z}_h$$

$$H = f(q, p, t) = f(q_1, \dots q_s, p_1, \dots p_s, t)$$

za Kl. meh. & Konz. sile $H = f(q, p) = E$

$$\dot{q}_k = \frac{\partial H}{\partial p_k} \qquad \dot{p}_k = -\frac{\partial H}{\partial q_k} \qquad k = 1, \dots s$$

uprinosi

$$\Rightarrow \quad q_k = q_k(q_1^\circ, \dots q_s^\circ, p_1^\circ, \dots p_s^\circ, t)$$

$$p_k = p_k(q_1^\circ, \dots q_s^\circ, p_1^\circ, \dots p_s^\circ, t) \qquad k = 1, \dots s$$

→ par (q, p) predstavlja 1 točku u $2s$-dim faznom prostoru, koja se giblje (za par eksplic. ovisi o t) i čini trajektoriju

→ u $t = 0$ (q°, p°) početni uvjet

Zadanih uvjeta ima neprebrojivo mnogo (za Klas. meh.) ⇒ pa i zadanih trajektorija (koje ovise zadane o (q°, p°) & $H(q, p, t)$)

$\vec{F} = -K\vec{r}$ (1 st. slob.) $\Rightarrow m\ddot{x} + Kx = 0 \quad \ddot{x} + \frac{K}{m}x = 0$, $\frac{K}{m} = \omega^2$

$x = A\sin\omega t + B\cos\omega t$

$\dot{x} = A\omega\cos\omega t - B\omega\sin\omega t$

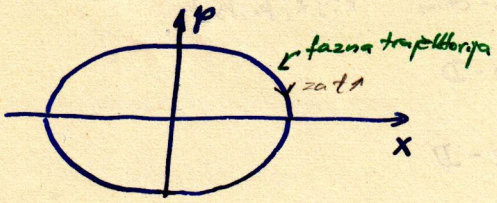
$t=0 \quad x=0 \quad \dot{x}=V \Rightarrow B=0 \quad A=\frac{V}{\omega} \Rightarrow x = \frac{V}{\omega}\sin\omega t$

$\dot{x} = V\cos\omega t$

Primjer: 1) Harmonički oscilator – 1 st. slobode gibanja $\Rightarrow$ fazna trajektorija = hiperploha

Klas. meh. & Konz. sile $\Rightarrow H = T + U = E \Rightarrow E = H = \frac{p^2}{2m} + \frac{m\omega^2}{2}x^2$

$T = \frac{m}{2}\dot{x}^2 = \frac{(m\dot{x})^2}{2m} = \frac{p^2}{2m}$



$\Rightarrow \frac{p^2}{2mE} + \frac{x^2}{\frac{2E}{m\omega^2}} = 1$

$-K\cdot x = -\frac{dU}{dx} \Rightarrow U = \frac{Kx^2}{2} + C$

$x=0 \; U=0 \Rightarrow U = \frac{K}{2}x^2$

$\Rightarrow U = \frac{m\omega^2}{2}x^2$

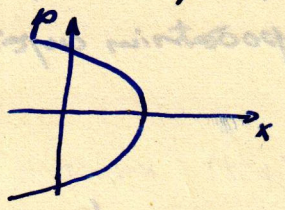
$\dot{x}(t) = x = \frac{V}{\omega}\sin\omega t$

$p = m\dot{x} = mV\cos\omega t$

$2mE = m^2V^2 \Rightarrow E = \frac{mV^2}{2}$

$\frac{2E}{m\omega^2} = \frac{V^2}{\omega^2} \Rightarrow E = \frac{m\omega^2}{2}$

2) Molekula u gravitacionom polju



Klas. meh. & Konz. sile $\Rightarrow H = T + U = E$

$\Rightarrow \frac{p^2}{2m} + mgx = E$

$x = \frac{E}{mg} - \frac{p^2}{2gm^2}$

– čestica se giba tako da se vrijednosti para (q, p) – njen reprezentant nalazi na faznoj trajektoriji:

→ **statističko promatranje:**

velik broj molekula $N \gg\gg 1 \Rightarrow S = K\cdot N$ (broj st. slobode 1 molekule)

$H = f(q, p, t)$ za Kl. meh. & Konz. sile $H = f(q, p) = E$ (*)

u principu iz (*)

$$q_k = q_k(q^\circ, p^\circ, t)$$
$$p_k = p_k(q^\circ, p^\circ, t) \qquad k = 1, \dots S \quad \} \; (**)$$

gdje je $(q^\circ, p^\circ) \equiv (q_1^\circ, \dots q_S^\circ, p_1^\circ, \dots p_S^\circ)$ poč. stanje tj. za $t=0$

(**) $\Rightarrow$ cijeli sistem (od N molek.) opisuje u vremenu fazna trajektorija (fazna točka) ≡ vrijed. stanje

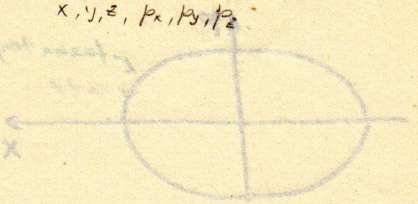
koja osim što ovisi o (*), ovisi i o (q°, p°)

$\Rightarrow$ za $\neq (q^\circ, p^\circ)$ dobivamo $\neq$ fazne trajektorije u ϕ prostoru (2-dim)

koje se međusobno razlikuju samo po tim poč. uvjetima

Statistički ansambl (Gibbs)

1-A molek.	$s=3$	translac.	6-dim x, y, z, p_x, p_y, p_z
(*) 2-A ~~o-o~~ $r=\text{const}$	$s=5$		10-D
2-A ⟷⟷	$s=6$		12-D



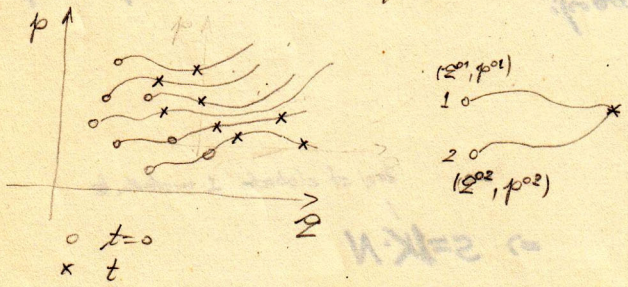
→ skup identičkih fizičkih sistema (N čestica, iste H fje.) koji se međusobno razlikuju po početnim uvjetima (q^0, p^0) zove se stat. ansambl

$$q_k = q_k(q^0, p^0, t) \qquad p_k = p_k(q^0, p^0, t) \qquad k = 1, \dots s$$

∀ pojedinačni sistem predstavljen je u ϕ prostoru (u nekom trenutku t_0) jednom faznom točkom

→ skup tih točaka u ϕ prostoru (u trenutku t) čini fazni ansambl

u principu $\phi \equiv$ faznom ansamblu u trenutku t



nemoguće jer bi to zahtijevalo unatoč $q^{01} \neq q^{02}$ $t=0$, $p^{01} \neq p^{02}$ u trenutku t:

$$q_k(q^{01}, p^{01}, t) = q_k(q^{02}, p^{02}, t)$$

$$p_k(q^{01}, p^{01}, t) = p_k(q^{02}, p^{02}, t) \quad \forall k = 1, \dots s$$

što je apsurdno jer to su jednoznačna rješenja sistema kanonskih jed.

≈ Kretanje faznih točaka ansambla slično je kretanju fluida

- razlika samo što se ne sudaraju, jer se fazne trajektorije ne mogu sjeći zbog principa kauzalnosti (≠ poč. uvjeti ne mogu dovesti do identičnih stanja sistema u daljoj evoluciji)

→ „fazni fluid" ⇒ hidrodinam. analogije

→ fazna gustoća - gustoća reprezentativnih stanja u točci $M(q_1, \dots q_s, p_1, \dots p_s) \equiv M(q, p)$

- u okolini M uočimo mali volumen $\Delta\phi = \prod_{i=1}^{s} \Delta q_i \, \Delta p_i$, u kojem u trenutku t ima ΔN faznih točaka (reprez. stanja)

$$\varrho(q, p, t) = \lim_{\Delta\phi \to 0} \frac{\Delta N}{\Delta\phi}$$

taj granični proces nemoguće shvatiti potpuno matematički tj. $\Delta\phi \to 0$ jer bi tada za $\varrho(q, p, t)$ dobili fju. koja u ovisnosti od q, p brzo oscilira između 0 i ∞. ?

- jer bi za $\Delta\phi \to 0$ $\quad \Delta N \to 1 \quad \Rightarrow \varrho(\Sigma, p, t) = \infty$

$\Rightarrow$ $\Delta\phi \to$ minimalnom „fizički ∞ malom" volumenu $\neq 0$

Kod običnog fluida koji bi sadržavao još dovoljno velik broj molekula

Kod „faznog fluida" da je znatno veći od elem. faznog ćelije $\Delta\phi_0 = h^s$

→ vjerojatnost da se reprez. točka (fazna točka) nađe u dif. elementu faznog prostora $\propto$ dif. broja faznih točaka u $d\phi$

$$dW = \varrho(\Sigma, p, t)\, d\phi$$

ustvari: $dW \propto dN = \varrho(\Sigma, p, t)\, d\phi$

- a konst. prop. ionako odmah iz normiranja vjerojatnosti

(*) je bilo za jednu molekulu, a nas zanima plin.

Plin

Energija sistema $H(\Sigma, p) = U$ $\qquad H(\Sigma, p) = E$ kl. mech. konz. sile

$$\dot{\Sigma}_k = \frac{\partial H}{\partial p_k}$$

$$\dot{p}_k = -\frac{\partial H}{\partial \Sigma_k}$$

rješ. kanonskih jb. $k = 1, 2, \ldots S$ $\quad (S \sim 10^{23})$ → točka u $2S$ dim faznom prostoru

$\Sigma_k = \Sigma_k(\Sigma^\circ, p^\circ, t)$

$p_k = p_k(\Sigma^\circ, p^\circ, t)$

Γ - prostor (Ehrenfest)

$2S$ dim fazni prostor

vjerojatnost da neko reprezentativno stanje nađemo unutar el. faznog volumena

$$dW = \varrho(\Sigma, p, t)\, d\phi \qquad d\phi = d\Sigma_1 \ldots d\Sigma_S\, dp_1 \ldots dp_S$$

↓ fja raspodjele

$$dW = \alpha \cdot dN = \alpha \cdot \varrho\, d\phi \qquad \alpha = \left[\int_\Gamma \varrho\, d\phi\right]^{-1} \quad \text{jer} \int_\Gamma dW = 1$$

↓ vjerojatnost da nasumce izabrana fazna točka (fizički sistem - stat. ansambl) iz čitavog Γ (tj. faznog ansambla) da je baš iz elem. faznog volumena $d\phi$ u okolini dane točke $M(\Sigma_1, \ldots \Sigma_S, p_1, \ldots p_S)$ faznog ansambla Γ

Teorem → za fju. raspodjele $\varrho(q, p, t)$

$$\frac{d\varrho}{dt} = \frac{\partial \varrho}{\partial t} + \sum_{k=1}^{S} \left(\frac{\partial \varrho}{\partial q_k} \cdot \dot{q}_k + \frac{\partial \varrho}{\partial p_k} \cdot \dot{p}_k \right)$$

u $2S$ dim. Γ-prostoru

jba. kontinuiteta:

$$\operatorname{div} \vec{j} + \frac{\partial \varrho}{\partial t} = 0 \quad (*)$$

Promjena gustoće faznih točaka mjeri se strujom faznih točaka koje izlaze ili ulaze u $d\phi$

radij vektor u Γ prostoru — boljе $\vec{\xi}_k$

$$\vec{R} = \sum_{k=1}^{S} \left[\vec{e}(q_k) \cdot q_k + \vec{e}(p_k) \cdot p_k \right]$$

$$\frac{d\vec{R}}{dt} = \sum_{k=1}^{S} \left[\vec{e}(q_k) \cdot \dot{q}_k + \vec{e}(p_k) \cdot \dot{p}_k \right]$$

gustoća struje $\quad \vec{j} = \varrho \frac{d\vec{R}}{dt} = \sum_{k=1}^{S} \left[\vec{e}(q_k) \cdot \varrho \dot{q}_k + \vec{e}(p_k) \varrho \dot{p}_k \right]$

poopćenje operatora div $\quad \operatorname{div} \vec{j} = \sum_{k=1}^{S} \left[\frac{\partial}{\partial q_k} (\varrho \dot{q}_k) + \frac{\partial}{\partial p_k} (\varrho \dot{p}_k) \right]$

$$\Rightarrow \operatorname{div} \vec{j} = \sum_{k=1}^{S} \left[\varrho \underbrace{\left(\frac{\partial \dot{q}_k}{\partial q_k} + \frac{\partial \dot{p}_k}{\partial p_k} \right)}_{\equiv 0 \ (*)} + \left(\frac{\partial \varrho}{\partial q_k} \cdot \dot{q}_k + \frac{\partial \varrho}{\partial p_k} \cdot \dot{p}_k \right) \right]$$

$$\frac{\partial}{\partial q_k} \left(\frac{\partial H}{\partial p_k} \right) + \frac{\partial}{\partial p_k} \left(-\frac{\partial H}{\partial q_k} \right) = 0$$

$$= \frac{d\varrho}{dt} - \frac{\partial \varrho}{\partial t}$$

(*) primjenjujemo Kanonske jbe. pr promatramo tot. vrem. promjenu fazne gustoće ϱ na faznoj trajektoriji.

$$(*) \Rightarrow \quad \frac{d\varrho}{dt} = 0 \qquad \varrho = \text{const.} \qquad \text{Liov. thm. 1851}$$

Fazna gustoća se ne mijenja s vremenom duž fazne trajektorije

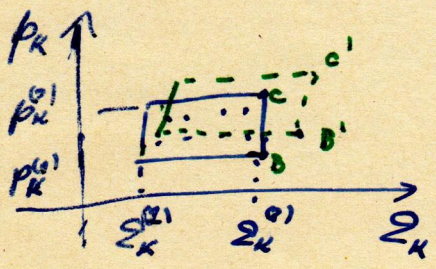
Fazne točke jednog ansambla (fizičkog sustava) čine inkompresibilan „fluid tzv." – (ako se u dotku kretanja ne mijenja nivelirana volumena nikoj točki $\Rightarrow$ gustoća konst.)

molekularni $\Delta\phi$ $\Rightarrow$

$$\Rightarrow \begin{cases} q_k^{(1)} \le q_k \le q_k^{(2)} \\ p_k^{(1)} \le p_k \le p_k^{(2)} \end{cases} \quad \forall k = 1, \dots s \qquad (*)$$

---

u



$$B\left(q_k^{(1)}, p_k^{(1)}\right) \quad B'\left(q_k^{(1)} + \dot{q}_k^{(1)} dt, \; p_k^{(1)} + \dot{p}_k^{(1)} dt\right)$$

→ budući je taj fazni volumen mali ⇒

$(**)$ $q_k^{(2)} - q_k^{(1)} \approx \Delta q_k \to dq_k \qquad k = 1, \dots s$

$\dot{q}_k^{(2)} - \dot{q}_k^{(1)} \approx \frac{d\dot{q}_k}{dq_k} \cdot \Delta q_k \to \frac{\partial \dot{q}_k}{\partial q_k} \cdot dq_k$ (kao gradijent po koordinati) $\overset{(*)}{=}$ samo zbog H-fje

$p_k^{(2)} - p_k^{(1)} \approx \Delta p_k \to dp_k$

$\dot{p}_k^{(2)} - \dot{p}_k^{(1)} \approx \frac{d\dot{p}_k}{dp_k} \cdot \Delta p_k \to \frac{\partial \dot{p}_k}{\partial p_k} dp_k$

$(*)$ $\dot{q}_k = \frac{\partial H(q_1, \dots p_s, t)}{\partial p_k}$ i pa ako H ovisi o svim koord.

ne može $\exists \; \frac{d\dot{q}_k}{dq_k} = \frac{d}{dq_k}\left(\frac{\partial H}{\partial p_k}\right)$ ne samo $\frac{\partial \dot{q}_k}{\partial q_k}$

jer faktor $\frac{\partial H}{\partial p_k}$ ovisi o svim koord. a pomaže

$$\varrho = \frac{dN}{d\phi} \quad \Rightarrow dN = \varrho d\phi$$

$$dW = \alpha \cdot dN = \alpha \varrho d\phi$$

$d\varrho$ - fazna gustoća vjerojatnosti -
ili fja. raspodjela vjerojatnosti.

odred. α

$$\int_\Gamma \alpha \varrho d\phi = 1 \quad \Rightarrow \alpha = \left[\int_\Gamma \varrho d\phi \right]^{-1}$$

gdje dW je vjerojatnost da nasumce izabrana fazna točka (stat. ansambl) iz čitavog Γ (tj. faznog ansambla) da je baš iz elem. faznog volumena $d\phi$ u okolini date točke (faznog prostora Γ)

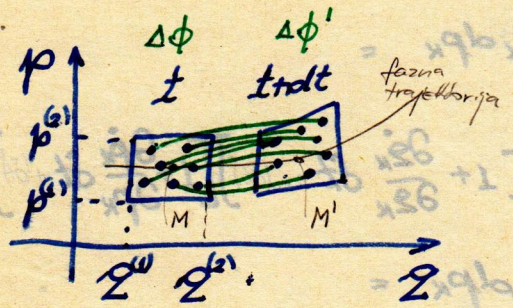
$M(q_1, \ldots q_s, p_1, \ldots p_s)$

!!! Originalno

$K = 3, 5, 6$

$Q \equiv (Q_1, \dots Q_s)$ $\quad s = K \cdot N$

$p \equiv (p_1, \dots p_s)$ $\quad t \to t+dt \Rightarrow M \to M'$



↑ fazna točka u $\phi(Q,p)$ prostoru $\Leftrightarrow$ istovrsni sistem (ansambl)

ΔN faznih točaka u $\Delta\phi$ elem. volum. u okolini $M(Q,p)$ na faznoj trajektoriji $\Leftrightarrow$ ΔN različitih ansambla sistema

$$\Delta\phi = (Q^{(2)} - Q^{(1)})(p^{(2)} - p^{(1)}) = \Delta Q \cdot \Delta p = \prod_{k=1}^{s} \Delta Q_k \cdot \Delta p_k$$

$$d\phi = = dQ \cdot dp = \prod_{k=1}^{s} dQ_k \cdot dp_k$$

$\delta_t = \delta$ vrem. varijacija $t, t+\delta t$ dviže fazne trajektorije (**)

$$\delta\, d\phi \overset{def.}{=} \prod_{k=1}^{s} dQ_k(t+\delta t)\, dp_k(t+\delta t) - \prod_{k=1}^{s} dQ_k(t)\, dp_k(t)$$

$$dQ_k(t+\delta t) = d\left\{ Q_k(t) + \underbrace{\frac{\dot Q_k(t)}{1!}}_{=\delta Q_k(t)} \delta t + \underbrace{\frac{\ddot Q_k(t)}{2!}}_{=\frac{\partial^2 Q_k(t)}{2!}} (\delta t)^2 + \dots \right\}$$

≈ 0 velič. drugog reda

$$dQ_k(t+\delta t) = dQ_k(t) + d\dot Q_k(t)\delta t + \dot Q_k(t)\, d(\delta t) + \dots$$

$=0$ jer $\frac{\partial(\delta t)}{\partial Q_k} dQ_k = 0$

$$\Rightarrow dQ_k(t+\delta t) = dQ_k(t) + \frac{\partial \dot Q_k(t)}{\partial Q_k} dQ_k \cdot \delta t$$

(*)

analogno:

$$dp_k(t+\delta t) = dp_k(t) + \frac{\partial \dot p_k(t)}{\partial p_k} dp_k \cdot \delta t$$

(*) $d\dot{q}_k(t) = \lim_{\Delta q_k \to 0} (\dot{q}_k^{(2)} - \dot{q}_k^{(1)}) \overset{\text{sr. wart.}}{=} \frac{d\dot{q}_k}{dq_k} \cdot dq_k = \frac{\partial \dot{q}_k}{\partial q_k} \cdot dq_k$

no bo dalej: $\dot{q}_k(t) = \frac{\partial H}{\partial p_k}$ $\quad H = H(q_1, q_2, \ldots, p_1, p_2, \ldots, t)$

$\Rightarrow$

$$\delta d\phi = \prod_{k=1}^{s} \left[dq_k + \frac{\partial \dot{q}_k}{\partial q_k} dq_k \delta t \right] \left[dp_k + \frac{\partial \dot{p}_k}{\partial p_k} dp_k \delta t \right] - \prod_{k=1}^{s} dq_k dp_k =$$

$$= \prod_{k=1}^{s} dq_k dp_k \left[1 + \frac{\partial \dot{q}_k}{\partial q_k} \delta t + \ldots (\delta t)^2 \right] \left[1 + \frac{\partial \dot{p}_k}{\partial p_k} \delta t + (\delta t)^2 \right] - \prod_{k=1}^{s} dq_k dp_k =$$

$$= \prod_{k=1}^{s} dq_k dp_k \cdot \prod_{k=1}^{s} \left[1 + \frac{\partial \dot{q}_k}{\partial q_k} \delta t \right] \left[1 + \frac{\partial \dot{p}_k}{\partial p_k} \delta t \right] - \prod_{k=1}^{s} dq_k dp_k =$$

$$= \prod_{k=1}^{s} dq_k dp_k \cdot \left[1 + \sum_{k=1}^{s} \left(\frac{\partial \dot{q}_k}{\partial q_k} + \frac{\partial \dot{p}_k}{\partial p_k} \right) \delta t + \left(\quad \right) (\delta t)^2 + \ldots \right] - \prod_{k=1}^{s} dq_k dp_k =$$

$$= \prod_{k=1}^{s} dq_k dp_k \cdot \left[\sum_{k=1}^{s} \frac{\partial \dot{q}_k}{\partial q_k} + \frac{\partial \dot{p}_k}{\partial p_k} \right] \delta t$$

(**) $\dot{q}_k = \frac{\partial H}{\partial p_k}$ $\quad \dot{p}_k = -\frac{\partial H}{\partial q_k}$

$$= \prod_{k=1}^{s} dq_k dp_k \left[\sum_{k=1}^{s} \left(\frac{\partial^2 H}{\partial p_k \partial q_k} - \frac{\partial^2 H}{\partial q_k \partial p_k} \right) \right] \delta t$$

$$= 0$$

$\Rightarrow$ $d\phi$ je niezmiennik kanoniczny na fazowej trajektorii

Objętościowy element dN fazowego płynu jest inwariantem ruchu na fazowej trajektorii

$$\Delta\phi' = \prod_{k=1}^{s} \left[\left(q_k^{(2)} - q_k^{(1)}\right) + \left(\dot{q}_k^{(2)} - \dot{q}_k^{(1)}\right) dt \right] \left[\left(p_k^{(2)} - p_k^{(1)}\right) + \left(\dot{p}_k^{(2)} - \dot{p}_k^{(1)}\right) dt \right]$$

zanemarimo član sa $(dt)^2$

$$\Delta\phi' = \prod_{k=1}^{s} \Big[\left(q_k^{(2)} - q_k^{(1)}\right)\left(p_k^{(2)} - p_k^{(1)}\right) + \left(p_k^{(2)} - p_k^{(1)}\right)\left(\dot{q}_k^{(2)} - \dot{q}_k^{(1)}\right) dt$$
$$+ \left(q_k^{(2)} - q_k^{(1)}\right)\left(\dot{p}_k^{(2)} - \dot{p}_k^{(1)}\right) dt + \dots \Big]$$

→ budući da su razlike u koordinatama vrlo male, možemo ih zamijeniti diferencijalima

$$\Delta\phi' = \prod_{k=1}^{s} \Big[\Delta q_k \cdot \Delta p_k + \Delta p_k \cdot \frac{\partial \dot{q}_k}{\partial q_k} \cdot \Delta q_k \cdot dt +$$
$$+ \Delta q_k \cdot \frac{\partial \dot{p}_k}{\partial p_k} \cdot \Delta p_k \cdot dt \Big]$$

$$\Delta\phi' = \prod_{k=1}^{s} \Delta q_k \cdot \Delta p_k \cdot \prod_{k=1}^{s} \left[1 + \frac{\partial \dot{q}_k}{\partial q_k} \cdot dt + \frac{\partial \dot{p}_k}{\partial p_k} \cdot dt \right]$$

zanemarimo član sa $(dt)^2$

ne odnosi se više Π

$$\Delta\phi' = \prod_{k=1}^{s} \Delta q_k \cdot \Delta p_k \cdot \left[1 + \sum_{k=1}^{s} \left(\frac{\partial \dot{q}_k}{\partial q_k} + \frac{\partial \dot{p}_k}{\partial p_k} \right) dt \right].$$

0 zbog Hamiltonovih jed. po kojima se gibaju molekule

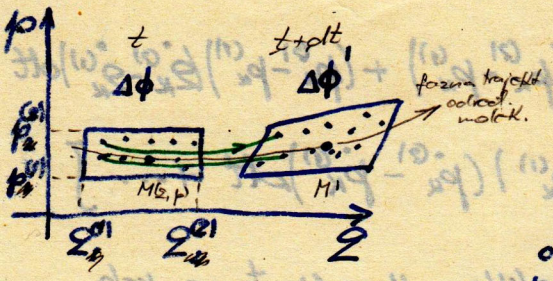
$$\Rightarrow \Delta\phi' = \prod_{k=1}^{s} \Delta q_k \cdot \Delta p_k = \Delta\phi$$

→ volumen u faznom prostoru, kojeg pokriva mnoštvo u gibanju, niti se povećava niti umanjuje

Molekule koje se kreću određuju uvijek jednako velik fazni volumen.

$q \equiv (q_1, \dots q_s)$ $\quad s = 3, 5, 6, \dots$

$p \equiv (p_1, \dots p_s)$



∀ fazna točka u $U(q,p)$ prostoru $\Leftrightarrow$ 1 molekula

ΔN faznih točaka u $\Delta\phi$ elem. volum. u okolini $M(q,p)$ na fazno trajektoriji: 1 određ. molek. $\Leftrightarrow$ ΔN različitih molekula

→ golemo mnoštvo čestica (molekula) koje se kreću u određenom času njihovi položaji i impulsi predstavljaju 1 dio μ-prostora (μ-prostor)

→ uzmimo u oko molekule koje se pri momentu t nalaze između položaja $q^{(1)}$ & $q^{(2)}$ i impulsa $p^{(1)}$ & $p^{(2)}$ (*1)

→ taj mali fazni volumen je

$$\Delta\phi = (q^{(2)} - q^{(1)})(p^{(2)} - p^{(1)}) = \Delta q \cdot \Delta p = \prod_{k=1}^{s} \Delta q_k \cdot \Delta p_k$$

$$= \prod_{k=1}^{s} (q_k^{(2)} - q_k^{(1)})(p_k^{(2)} - p_k^{(1)})$$

→ molek. se kreću i u kasnijem trenutku $t+dt$ predstavat će neki drugi fazni volumen koji neće biti više pravokutnik ("po obliku") ! (postavo da $\Delta N \to \infty$)

→ dobijamo ga ako uzmemo točke u koje su stigli vrhovi (tj. molekule koje su se nalazile u vrijednostima generalisanih koordinata u trenutku t)

$$\Delta\phi' = \prod_{k=1}^{s} \left[q_k^{(2)} + \dot{q}_k^{(2)} dt - q_k^{(1)} - \dot{q}_k^{(1)} dt \right] \left[p_k^{(2)} + \dot{p}_k^{(2)} dt - p_k^{(1)} - \dot{p}_k^{(1)} dt \right]$$

6. Vrh →

$\propto dN$

$dW = \alpha\, g\, d\phi$ ⇒ jednako veliki fazni volumeni su jednako vjerojatni.

pri kretanju (po faznoj trajektoriji) u apstraktnom Γ-prost.

(?) da li samo za idealni plin

Prodegnuto na μ-prostor (μ-prostor) = fazni prostor molekule $2s$-dim. $s = 3, 5, 6, \ldots$

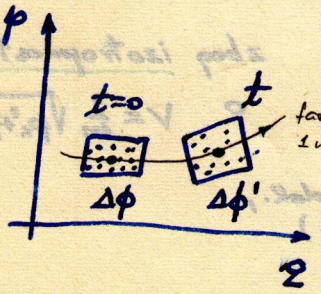
Ako u plinu nema međumolekularne interakcije (*)

$$H = \sum_{i=1}^{N} H_i = U$$

- u Γ prostora veliko mnoštvo fizičkih sistema (# od N molek). ⊡ el. Γ prost.
  # točka predstavlja ekvival. fizički sistem (ansambl), ali se ≠ poč. uvjetima
- u μ-prostoru molekule su ekvivalentni sistemi (zadnji fizički sist.) jer $H(q,p) = E$ ako vrijedi (*) & kl. mehanske sile
  s-st. slobode $s = 3, 5, 6, \ldots$ $(q_1, \ldots q_s, p_1, \ldots p_s)$ a ≠ poč. uvjeta

⇒ # molekula predst. točkom u μ-prost ⊡ · eU

$$g = \lim_{\Delta\phi \to 0} \frac{\Delta N}{\Delta \phi}$$ gustoća molekula u μ-prost.



$g = \text{const.}$ na faznoj trajektoriji 1 molekule, dakle točkom mnoma (odnosno ansambl)

$g(q, p, t)$

ako $\Delta\phi = \Delta\phi'$ ⇒ $g(q(0), p(0), 0)\,\Delta\phi = g(q(t), p(t), t)\,\Delta\phi'$

$\Delta W(0) = \Delta W(t)$

- isti broj molekula
- jednako veliki fazni volumeni su jednako vjerojatni

nalaz sa papira →

(1) Mnoštvo molekula zapremit će u gibanju sve moguće, ali jednako velike fazne volumene.
Ako točkom mnoma načinimo u jednako velikim volumnim elementima faznog prostora (⇒ sigurno da u svima ekvatorima koji predstavljaju broj molekula ≠ usmjerenje (H))
jednako velik broj molekula ⇒ jednako veliki fazni volumni elementi [a priori]
jednako vjerojatni ⇐ Liouv. teor.

→ a priorna vjerojatnost – vrijedi se još o termički uravnoteženom sistemu
(plin – atmosfera ima ≠ gustoću zbog term. ravnot. plina u gravit. polju)
– a priori, neovisno se još za temperaturu i energiju plina, # točka u prostoru predstavlja očito jednako vjerojatan položaj molekule

⇒ za sistem u term. ravnoteži, gdje $E_{molekule} \approx \bar{E}$ ⇒ vjerojatnost da se molekula nalazi u $dx\,dy\,dz\,dp_x\,dp_y\,dp_z$ zavisi još i o energiji koju ima u tom stanju ⇒ $f(E)\,dx\,dy\,dz\,dp_x\,dp_y\,dp_z$

→ Fazni prostor μ razdijelimo u ćelije jednakog volumena.
A priorna vjerojatnost da se molekula nalazi u nekoj ćeliji jednaka je za sve ćelije
$\forall$ ćeliji pripada izvjesna energija, koja je određena koordinatama x, y, z i impulsima p_x, p_y, p_z ćelije

Energije tih ćelija možemo nanijeti kao diskontinuum $E_1, E_2, E_3, \ldots$

Kako se čestice, koje se nalaze u termičkoj ravnoteži, raspodjeljuju na te energije?
$\Leftarrow$ odredit gustoće vjerojatnosti s kojom će se raspodijeliti

Razlika: apriorna vjerojatnost

$dW = g\, d\phi$

$g = \text{const}$

vjerojatnost (sistema u term. ravnoteži) elementa $d\phi$ da se nalazi molek.

$dW = \underbrace{f(E)}_{g(q,p,t)}\, g\, d\phi$

$g(q,p,t)$ - fja raspodjele

tenzor

$\frac{dg(q,p,t)}{dt} \equiv 0$

Maxwell-ova raspodjela

1-A plin idealni (za višeatomne dopuštamo transl. težišta)

→ nema vanjskih sila $\Rightarrow E = \frac{mv^2}{2}$

$g(q,p,t) \to g(p_x, p_y, p_z)$

nema

$\Rightarrow g = g(v)$

zbog izotropnosti samo o $v = \frac{1}{m}\sqrt{p_x^2 + p_y^2 + p_z^2}$

② ako je samo ako je idealni plin

Idealan plin → μ prostor (što vrijedi za 1 molek., vrijedi za μ)

Pretp

1. Vjeroj. brzine u intervalu $v_x \quad v_x + dv_x$ (1)

$dW_x = g_x(v_x)\, dv_x$

$v_y \quad v_y + dv_y$ (2)

$dW_y = g_y(v_y)\, dv_y$

$v_z \quad v_z + dv_z$ (3)

$dW_z = g_z(v_z)\, dv_z$

2. Vjerojatnost brzine unutar faznog volumena $\vec{v} \quad \vec{v} + d^3v$ (4)

$dW = g(v)\, d^3v$

$d_1W = g(v) d^3v \cdot dx dy dz$ vjeroj. da je molekula unutar

$\Rightarrow d_1W = dW \cdot dx dy dz$ $\Rightarrow dW$ vjerojatnost brzine

$x \quad x+dx$
$y \quad y+dy$
$z \quad z+dz$

$v_x \quad v_x + dv_x$
$v_y \quad v_y + dv_y$
$v_z \quad v_z + dv_z$

$\Leftrightarrow \vec{v} \quad \vec{v} + d^3v$

ili da promatramo samo fazni prostor impulsa (brzine) molekule

(1), (2) & (3) nezav. događaji, a (4) se sastoji od njih $\Rightarrow$

$$dW = dW_x\, dW_y\, dW_z$$

$$g(V)\, dV_x dV_y dV_z = g_x(V_x)\, g_y(V_y)\, g_z(V_z)\, dV_x dV_y dV_z \qquad V = \sqrt{V_x^2 + V_y^2 + V_z^2}$$

$$\Rightarrow \quad g(V) = g_x(V_x)\, g_y(V_y)\, g_z(V_z)$$

$$\ln g = \ln g_x + \ln g_y + \ln g_z \quad / \frac{\partial}{\partial V_x}$$

$$\frac{\partial}{\partial V_x} \ln g(V) = \frac{d}{dV_x} \ln g_x = \frac{\frac{dg_x}{dV_x}}{g_x}$$

$\phi[V(V_x)]$

$$\frac{\partial \phi[V(V_x)]}{\partial V_x} = \frac{\partial \phi}{\partial V} \cdot \frac{\partial V}{\partial V_x} = \frac{d\phi}{dV} \cdot \frac{\partial V}{\partial V_x}$$

$V^2 = V_x^2 + V_y^2 + V_z^2 \qquad 2V \frac{\partial V}{\partial V_x} = 2V_x \quad \Rightarrow \quad \frac{\partial}{\partial V_x} = \frac{V_x}{V} \cdot \frac{\partial}{\partial V}$

$$\Rightarrow \quad \frac{V_x}{V} \frac{1}{g} \frac{dg}{dV} = \frac{1}{g_x} \frac{dg_x}{dV_x}$$

$$\Rightarrow \quad \frac{1}{g \cdot V} \frac{dg}{dV} = \frac{1}{g_x(V_x) V_x} \frac{dg_x(V_x)}{dV_x} = \frac{1}{g_y V_y} \frac{dg_y}{dV_y} = \frac{1}{g_z V_z} \frac{dg_z}{dV_z} = \text{?} = -a$$

($g_x(V_x)$ ... fja samo od V_x)

$a > 0$

ta forma je sačuvana, zbog nezavisnosti. Komponenata vrijedi samo ako je konstanta $(-a)$

$$\Rightarrow \frac{dg_x(V_x)}{dV_x} = -a\, g_x V_x \quad \Rightarrow \quad \frac{dg_x}{g_x} = -a\, V_x dV_x \qquad \ln g_x - \ln A_x = -a \frac{V_x^2}{2}$$

$$\Rightarrow \quad \underline{g_x(V_x) = A_x e^{-\frac{a V_x^2}{2}}}$$

$dW = g\, d\phi \qquad \int dW = 1 \quad \Rightarrow \int g\, d\phi = 1$

↖ za nezavisne događaje kao ovi

$$\rightarrow \int_{-\infty}^{\infty} g_x(V_x) dV_x = 1 \qquad A_x \int_{-\infty}^{\infty} e^{-\frac{a V_x^2}{2}} dV_x = 1$$

$$t = \sqrt{\frac{a}{2}} V_x \qquad dt = \sqrt{\frac{a}{2}} dV_x \quad \Rightarrow \quad A_x \sqrt{\frac{2}{a}} \underbrace{\int_{-\infty}^{\infty} e^{-t^2} dt}_{=\sqrt{\pi}} = 1$$

$\Gamma(x) \overset{def}{=} \int_0^{\infty} e^{-y} y^{x-1} dy \qquad x > 0 \Rightarrow \Gamma(x+1) = x\Gamma(x)$ (za $x \leq 0$ def. ima No)

$\Gamma(n+1) = n!$

$\Gamma\left(\frac{2n+1}{2}\right) = \frac{(2n)!}{2^{2n} n!} \sqrt{\pi}$ jer $\Gamma\left(\frac{1}{2}\right) = \sqrt{\pi}$

$$\sqrt{\pi} = \Gamma\left(\tfrac{1}{2}\right) = \int_0^{\infty} e^{-y} y^{-\frac{1}{2}} dy = \int_0^{\infty} e^{-t^2} t^{-1} 2t\, dt = 2\int_0^{\infty} e^{-t^2} dt = \int_{-\infty}^{\infty} e^{-t^2} dt$$

$y = t^2 \qquad dy = 2t\, dt$

$y = \infty \Rightarrow t = \pm\infty$

$\Gamma(x) \overset{def}{=} \int_0^\infty e^{-y} y^{x-1} dy \overset{y=t^2}{=} 2\int_0^\infty e^{-t^2} t^{2x-1} dt$ za $x>0$ konv. $\quad 2x-1=n$

$\Rightarrow \Gamma\left(\frac{n+1}{2}\right) = 2\int_0^\infty t^n e^{-t^2} dt = \int_{-\infty}^\infty t^n e^{-t^2} dt$

od interesa **neN** paran $n=0,2,4,6,\dots$

$\Gamma(x+1) = x\Gamma(x)$ svojstvo za $x>0$

$\Gamma\left(\frac{n+1}{2}\right) = \Gamma\left(\frac{(n-2)+1}{2}+1\right) = \frac{n-1}{2}\Gamma\left(\frac{(n-2)+1}{2}\right)$

$\Rightarrow \int_{-\infty}^\infty t^n e^{-t^2} dt = \frac{n-1}{2}\int_{-\infty}^\infty t^{n-2} e^{-t^2} dt$

$\sqrt{\pi} = \Gamma\left(\frac{1}{2}\right) = \Gamma\left(\frac{0+1}{2}\right) = \int_{-\infty}^\infty e^{-t^2} dt$

$\Rightarrow A_x = \sqrt{\frac{a}{2\pi}} \quad / \cdot \quad g_x(v_x) = \sqrt{\frac{a}{2\pi}} e^{-\frac{a v_x^2}{2}}$

analogno $g_y(v_y)$ & $g_z(v_z)$

$g(v) = g_x(v_x)\, g_y(v_y)\, g_z(v_z) = \left(\frac{a}{2\pi}\right)^{3/2} e^{-\frac{a(v_x^2+v_y^2+v_z^2)}{2}}$

$\Rightarrow g(v) = \left(\frac{a}{2\pi}\right)^{3/2} e^{-\frac{a}{2}v^2}$ **Maxwell 1860**

- da smo stavili samo (a) $a>0$ kod normiranja vjerojatnosti dobili bi $A_x \int_{-\infty}^\infty e^{-\frac{a v_x^2}{2}} dv_x = 1$

odnosno za $t = \sqrt{\frac{a}{2}} v_x \Rightarrow A_x \sqrt{\frac{2}{a}} \int_{-\infty}^\infty e^{t^2} dt = 1$ ali $\int_{-\infty}^\infty e^{t^2} dt$ divergira

(μ' implicira dio μ prostora)

$\to \int_{\mu'} dW = \int_{\mu'} g(v)\, d^3v = \int_{-\infty}^\infty\int_{-\infty}^\infty\int_{-\infty}^\infty g(v)\, dv_x dv_y dv_z = \int_{-\infty}^\infty\int_{-\infty}^\infty\int_{-\infty}^\infty \left(\sqrt{\frac{a}{2\pi}}\right)^3 e^{-\frac{a}{2}(v_x^2+v_y^2+v_z^2)} dv_x dv_y dv_z = \int_{-\infty}^\infty \sqrt{\frac{a}{2\pi}} e^{-\frac{a}{2}v_x^2} dv_x \int_{-\infty}^\infty \sqrt{\frac{a}{2\pi}} e^{-\frac{a}{2}v_y^2} dv_y \int_{-\infty}^\infty \sqrt{\frac{a}{2\pi}} e^{-\frac{a}{2}v_z^2} dv_z = 1$

nemožemo pisati $\int_{\mu'} dW = \int_0^\infty g(v) dv$ jer je dv vjerojatnost da se brzina molekule nalazi u $v, v+dv$, a ne u $\vec{v}, \vec{v}+d^3v$

→ **možemo naći srednju vrijednost fiz. veličine $G(v)$**

operacija $\bar{x} = \sum_{i=1}^n x_i \cdot p_i$ za $y=f(x)$ $\quad \bar{y} = \lim_{n\to\infty} \sum_{i=1}^n y_i \cdot p_i = \lim_{n\to\infty} \sum_{i=1}^n f(a+i\cdot\Delta x)\cdot\varphi(a+i\cdot\Delta x)\Delta x = \int_a^b f(x)\varphi(x)dx = \int_a^b f(x)d\varphi$

$\bar{G}(v) = \int_{\mu'} G(v)\, dW$

$= \int_{\mu'} G(v)\, g(v)\, d^3v$

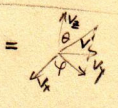
$= 4\pi \int_0^\infty G(v) g(v) v^2 dv$

$\Rightarrow \bar{G}(v) = 4\pi \left(\frac{a}{2\pi}\right)^{3/2} \int_0^\infty G(v) e^{-\frac{a}{2}v^2} \cdot v^2 dv$

za $\forall$ fiz. veličinu $G(v)$

fja $G(v)$ ovisi samo o iznosu v, pa integracija $\int_{-\infty}^\infty\int_{-\infty}^\infty\int_{-\infty}^\infty \dots dv_x dv_y dv_z$ po μ' prostoru integrirat ćemo po ljusci $d^3v = 4\pi v^2 dv$

Zaprav: $\int_{\mu'} G\left(\sqrt{v_x^2+v_y^2+v_z^2}\right) g\left(\sqrt{v_x^2+v_y^2+v_z^2}\right) dv_x dv_y dv_z =$



$v_x = v\sin\theta\cos\varphi \quad v_y = v\sin\theta\sin\varphi \quad v_z = v\cos\theta$

$\Rightarrow v^2 = v_x^2 + v_y^2 + v_z^2$

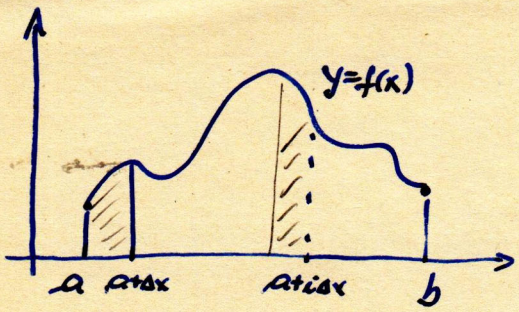
$= \int_{\mu'} G(v) g(v) \cdot \left|\frac{\partial(v_x, v_y, v_z)}{\partial(v,\theta,\varphi)}\right| dv\, d\theta\, d\varphi =$

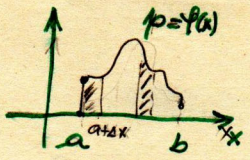
$\frac{\partial(v_x, v_y, v_z)}{\partial(v,\theta,\varphi)} = \begin{vmatrix} \frac{\partial v_x}{\partial v} & \frac{\partial v_x}{\partial\theta} & \frac{\partial v_x}{\partial\varphi} \\ \frac{\partial v_y}{\partial v} & \frac{\partial v_y}{\partial\theta} & \frac{\partial v_y}{\partial\varphi} \\ \frac{\partial v_z}{\partial v} & \frac{\partial v_z}{\partial\theta} & \frac{\partial v_z}{\partial\varphi} \end{vmatrix} = v^2\sin\theta$

$= \int_0^\infty \int_0^\pi \int_0^{2\pi} G(v) g(v) \cdot v^2 \sin\theta\, dv\, d\theta\, d\varphi =$

$= 2\pi \int_0^\infty G(v) g(v) v^2 dv \cdot \int_0^\pi \sin\theta\, d\theta = 4\pi \int_0^\infty G(v) g(v) v^2 dv$

originalno !!!





p

$\frac{b-a}{n} = \Delta x$

$i=1 \quad y_1 = f(a+1\Delta x) \quad \cdots \quad p_1 = \varphi(a+1\cdot\Delta x)\cdot\Delta x$

$i=2 \quad y_2 = f(a+2\cdot\Delta x) \quad \cdots \quad p_2 = \varphi(a+2\cdot\Delta x)\cdot\Delta x$

$\vdots$

$i \quad y_i = f(a+i\cdot\Delta x) \quad \cdots \quad p_i = \varphi(a+i\cdot\Delta x)\cdot\Delta x$

$\vdots$

$i=n \quad y_n = f(a+n\cdot\Delta x) \quad \cdots \quad p_n = \varphi(a+n\cdot\Delta x)\cdot\Delta x$

$f(b) \qquad\qquad \varphi(b)$

$p_1 + p_2 + \cdots p_n = 1 \qquad n\to\infty \Rightarrow \Delta x \to 0$

$$\lim_{n\to\infty} \sum_{i=1}^{n} \varphi(a+i\cdot\Delta x)\cdot\Delta x = 1$$

$$\int_a^b \underbrace{\varphi(x)\cdot dx}_{dp} = 1$$

$$\bar{y} = \lim_{n\to\infty} \sum_{i=1}^{n} y_i \cdot p_i = \lim_{n\to\infty} \sum_{i=1}^{n} f(a+i\cdot\Delta x)\cdot\varphi(a+i\cdot\Delta x)\cdot\Delta x$$

$$\Rightarrow \bar{y} = \int_a^b f(x)\underbrace{\varphi(x)dx}_{dp} = \int_a^b f(x)\,dp$$

$\frac{3}{2} \cdot \frac{1}{2} \cdot \sqrt{\pi}$

Specijalno: $G(V) = E = \frac{mv^2}{2}$

$t = \sqrt{\frac{a}{2}}\, v \quad \Rightarrow v^4 = \left(\frac{2}{a}\right)^2 \cdot t^4$

$dV = \left(\frac{a}{2}\right)^{1/2} \cdot dt$

$$\bar{E} = 4\pi \left(\frac{a}{2\pi}\right)^{3/2} \cdot \frac{m}{2} \int_0^\infty e^{-\frac{a}{2}v^2} \cdot v^4 dv = 4\pi \left(\frac{a}{2}\right)^{3/2} \cdot \pi^{-3/2} \cdot \frac{m}{2} \int_0^\infty e^{-t^2} \cdot t^4 \cdot \left(\frac{2}{a}\right)^{5/2} dt =$$

$$= 2\pi m \left(\frac{a}{2}\right)^{-1} \cdot \pi^{-3/2} \int_0^\infty e^{-t^2} \cdot t^4 dt$$

$$= 2\pi m \cdot \frac{2}{a} \cdot \pi^{-1} \cdot \frac{1}{\pi} \int_0^\infty e^{-t^2} \cdot t^4 dt$$

$$2\int_0^\infty e^{-t^2} \cdot t^4 dt = \Gamma\left(\frac{4+1}{2}\right) = \Gamma\left(\frac{5}{2}\right) = \Gamma\left(\frac{2 \cdot 2+1}{2}\right) =$$

$$= \frac{4!}{2^4 \cdot 2!} \sqrt{\pi} \qquad 4! = 2 \cdot 3 \cdot 4 \qquad 2^4 = 2 \cdot 2 \cdot 2 \cdot 2$$

$$= \frac{3}{4}\sqrt{\pi}$$

$$= \frac{2\pi m}{a\sqrt{\pi}} \cdot \frac{3}{4_2}\sqrt{\pi} = \underline{\frac{3m}{2a}}$$

Komparacijom sa: $\bar{E} = \frac{3}{2} kT \Rightarrow$

$$\underline{a = \frac{m}{kT}}$$

$$\Rightarrow \underline{g(V) = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}}}$$

gustoća vjerojatnosti da je brzina u $\vec{V}, \vec{V}+d^3\vec{V}$

$$\bar{G}(V) = 4\pi \int_0^\infty G(V) g(V) \cdot v^2 dv = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty G(V) \cdot e^{-\frac{mv^2}{2kT}} \cdot v^2 dv$$

$$\rightarrow \bar{G}(V) = \int_0^\infty G(V) \cdot P(V) dV$$

vjerojatnost da je brzina nalazi između $V, V+dV$

situacija: trodimenz problem
kao jednodimenzionalni

$$P(V) = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mv^2}{2kT}} \cdot V^2$$

oblik je.

gustoća vjerojatnosti da je brzina (po iznosu) u $V, V+dV$

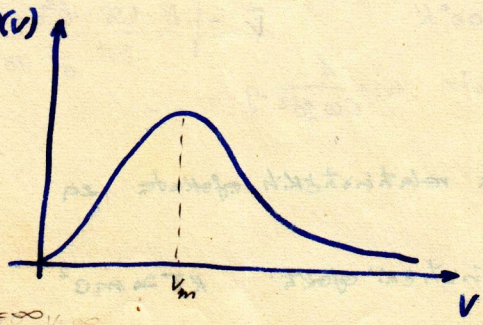
$$\lim_{x\to\infty} \frac{x^2}{e^{x^2}} = \lim_{x\to\infty} \frac{2x}{2x e^{x^2}} = 0$$

→ najvjerojatnija brzina

$$\frac{dP(V)}{dV} = 0$$

$$-\frac{m}{2kT} e^{-\frac{mv^2}{2kT}} \cdot 2V^3 + e^{-\frac{mv^2}{2kT}} \cdot 2V = 0$$

$$-2 \cdot V \cdot e^{-\frac{mv^2}{2kT}} \left(\frac{m}{2kT} V^2 - 1\right) = 0$$



infleksija $V=0$
$\Rightarrow$ ekstrem. $V=\infty, V = \sqrt{\frac{2kT}{m}}$

$$\underline{V_m = \sqrt{\frac{2kT}{m}}}$$

- najvjerojatnija brzina

$$\bar{E} = \frac{m\bar{v}^2}{2}$$

→ **srednja vrijednost kvadrata brzine**

$$\bar{v}^2 = \frac{2}{m}\bar{E} = \frac{2}{m}\cdot\frac{3}{2}kT$$

$$\boxed{\bar{v}^2 = \frac{3kT}{m}} \qquad \sqrt{\bar{v}^2} = \sqrt{\frac{3kT}{m}}$$

→ **srednja vrijednost brzine**

$$G(v) = v \qquad \bar{G}(v) = \int_0^\infty G(v)\cdot P(v)\,dv$$

$$\bar{v} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty e^{-\frac{m}{2kT}v^2}\cdot v^3\,dv \qquad \int_0^\infty e^{-t^2}\cdot\left(\frac{2kT}{m}\right)^{3/2}\cdot t^3\left(\frac{2kT}{m}\right)^{1/2}\cdot dt$$

$$= 4\pi\cdot\pi^{-3/2}\cdot\left(\frac{m}{2kT}\right)^{3/2}\cdot\left(\frac{2kT}{m}\right)^{1/2}\int_0^\infty t^3\cdot e^{-t^2}dt = 4\pi^{-1/2}\cdot\left(\frac{2kT}{m}\right)^{1/2}\int_0^\infty t^3\cdot e^{-t^2}dt$$

$$\Gamma(x) \overset{dot}{=} \int_0^\infty e^{-y}\cdot y^{x-1}dy = 2\int_0^\infty e^{-t^2}\cdot t^{2x-1}dt \qquad 2x-1 = n$$

$$\Rightarrow \Gamma\left(\frac{n+1}{2}\right) = 2\int_0^\infty e^{-t^2}\cdot t^n\,dt$$

odzintegrira se $n \in N$ neparan $1, 3, 5, \ldots$

$\Gamma(n+1) = n!$

$\Gamma(x+1) = x\Gamma(x)$ za $x > 0$

$\Gamma\left(\frac{n+1}{2}\right) = \Gamma\left(\frac{(n-2)+1}{2}+1\right) = \frac{n-1}{2}\Gamma\left(\frac{(n-2)+1}{2}\right)$

$$\Rightarrow 2\int_0^\infty e^{-t^2}\cdot t^n\,dt = \frac{(n-1)}{2}2\int_0^\infty e^{-t^2}\cdot t^{n-2}\,dt$$

$$2\int_0^\infty e^{-t^2}\cdot t\,dt = \Gamma(1) = 1$$

$\times\ \Gamma(1) = \int_0^\infty e^{-y}dy = -(0+1) = 1$

$$\Rightarrow 2\int_0^\infty t^3 e^{-t^2}dt = \frac{3-1}{2}\cdot 2\int_0^\infty t\cdot e^{-t^2}dt = 1\cdot 1 = 1$$

$$\boxed{\bar{v} = \sqrt{\frac{8kT}{\pi m}}}$$

Odnosi:

$$v_m : \bar{v} : \sqrt{\bar{v}^2} = 1 : \frac{2}{\sqrt{\pi}} : \sqrt{\frac{3}{2}} = 1 : 1{,}13 : 1{,}22$$

sobna temp:

$T = 300\,°K$

1-A He-plin $m = \frac{4}{6{,}02\cdot 10^{23}}\,g$

$$\bar{v} = \sqrt{\frac{8\cdot 1{,}38\cdot 10^{-16}\,erg\,st^{-1}\cdot 3\cdot 10^2\,st}{3{,}14\cdot\frac{4}{6}\cdot 10^{23}\,g}} = \sqrt{4{,}138\cdot 3\cdot 10^9}\ cm/s = 10^4\cdot 12\ cm/s \approx 10^5\,m/s$$

$\bar{v} \approx$ Km/s

→ nema relativističkih efekata za $\bar{v} \ll c \Rightarrow kT \ll m_0c^2$

→ relativistički efekti $kT \simeq m_0c^2$ $\Rightarrow T_{rel.} \simeq \frac{m_0c^2}{k} = \frac{4}{6{,}02}\cdot 10^{-23}\cdot 9\cdot 10^{16}\cdot\frac{1}{1{,}38}\cdot 10^{16}\,st \approx 6\cdot 10^9\,K$ (10^{13})

Generalizacija Maxwell. raspodjele

1. molekule nisu 1-A
2. ne djeluju vanjske sile
3. nema međudjelovanja (idealni plin) u sistemu

Kod Maxw. $E = \frac{mv^2}{2}$ $\qquad S(E) \sim e^{-\frac{E}{kT}}$

akumulacija

Boltzmann-ova raspodjela

→ sistem mnoštva č. u klas. režimu ako $\frac{V}{Nh^3}(mKT)^{3/2} \gg 1$ uvjet za klasičnu statistiku

→ Fazni prostor molekule (μ s - st. slobode ⇒ $d\phi = dq_1 \dots dq_s\, dp_1 \dots dp_s$

Fazni prostor cijelog plina Γ $S = 2s \cdot N$

Vjerojatnost $dW = g(q,p,t)\,d\phi$ normirano $\int dW = 1$ „sigurnost"

→ za fju. raspodjele vrijedi Liov. tm. $\frac{dg}{dt} = 0$

→ 1-A plin Maxw. raspodjela: $g(v) = \left[\frac{m}{2\pi KT}\right]^{3/2} e^{-\frac{mv^2}{2kT}}$ gustoća vjeroj. za $\vec{v}, \vec{v}+d^3v$

– generalizirati za čestice izvan vanjskih sila (općenitije uz djelov. vanjskih sila), ali još uvijek promatrano idealan plin – nema međudjelovanja čestica sistema

$g(v) \sim e^{-\frac{mv^2}{2}/KT}$ & $E = \frac{mv^2}{2}$ ⇒ $g(E) \sim e^{-\frac{E}{KT}}$

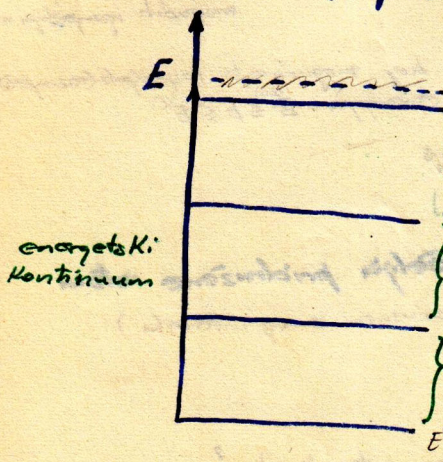
dali i ako E nije samo kin. energija, već rotacija i energ. vanjskog polja

→ promatramo term. uravnotežen sistem

V, $N_{(molek)}$, T → po kojem zakonu su čestice tog sistema raspoređene po energijama?

→ promatramo: idealan plin

(μ-prostor – #molek. točkom



$E_i = E^{(i)} - E^{(i-1)}$; N_3, N_2, N_1 ; g_3, g_2, g_1

broj čestica koje su raspoređene po toj energiji tom intervalu energije

broj kvantnih ćelija

točnije

$E_1, E_2, \dots E_i, \dots$

niz energija diskontinuiran

tj. razlika između susjednih energija je konačna

$E_i \equiv (E^{(i)}, E^{(i)} + \Delta E^{(i)})$

1° Energetske slojeve reprezentiramo energetskim (intervale) (zapravo energetski intervali) nivoima → klas. kontinuum

→ moguće energije molekula čine niz $E_1, E_2, E_3, \dots$ razmak može biti

← dako sitan da diskontinuitet iščezava : tj. gusti niz ≡ kontinuitet

recimo $\Delta E \ll h$

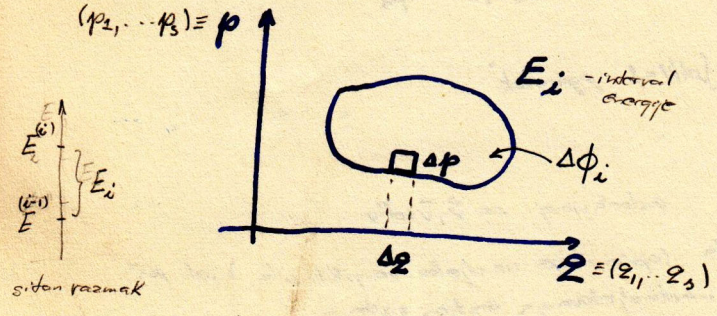
uzimamo razmak među nivoima samo da bismo lakše računali → matem. dosjetka, a ne korak ka kvantnoj fizici.

2° E_i – tom nivou → N_i čestica

3° sadrži: Kvantna fizika

za konjugirano parove $\Delta q_k \cdot \Delta p_k \simeq h$ $k = 1, \dots s$ za $\forall$ molekulu
(sve stupnji slobode)

u faznom prost. molekule - μ



→ Koliko različitih kvantnih stanja imamo u itom E_i

→ intervalu energije E_i pridružujemo taj dio faznog prost.

→ različita kv. stanja možemo razlikovati na sitnim Δq & Δp

relacija neodr. => sitan fazni pr. razbijan u ćelije $\Delta q \cdot \Delta p$

=> za s st. slobode fazna ćelija $\Delta\phi = h^s$
za $s = 1$ jednodim. gibanje $\Delta\phi = \Delta q \cdot \Delta p = h$

naime: E_i je interval energije (istina vrlo mali, trebali bi pisati $E_i = E^{(i)} - E^{(i-1)}$) ΔE_i

$E = E(q, p)$ energija 1 molekule => $E^{(i-1)} \le E \le E^{(i)}$ (*)

Klas. fizika => ∞ mnogo parova (q, p) da bude zadovoljeno (*), tj. ∞ mnogo mogućnosti
∞ mnogo mogućih faznih ćelija
mogućih razmještaja molekula

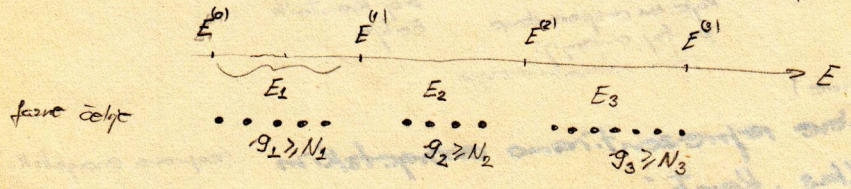
Kvantna fizika => Konačan broj vrijednosti parova (q, p)
koji se mogu razlikovati → Konačan broj mogućnosti raspodjele (razmještaja) molekula energija $E^{(i-1)} \le E \le E^{(i)}$

⇕

Konačan broj razlučivih faznih ćelija $\Delta q \cdot \Delta p = h^s$
$\forall$ ćeliji pripada izvjesna energija $E(q, p)$

4° $E_i \leftrightarrow g_i$ (interval ⇕) - broj različitih kvant. faznih ćelija pridružene istom energetskom nivou (zapravo sićušnom energ. intervalu)
- faktor degeneracije

→ Kako će se čestice raspodijeliti po energ. nivoima (malim energ. intervalima)?



→ Koja je raspodjela molek. (čestica) po energ. nivoima (malim energ. intervalima) najvjerojatnija!
tj. ima najveću stat. težinu
očito, način popunjavanja koji sadrži najviše mogućnosti - najveći broj permutacija

prirodno: $\forall$ permutaciji pridružimo jednaku stat. težinu - vjerojatnost, pa
ranije razloga misliti, da bi neka permutacija molekula bila vjerojatnija od druge

B - broj različitih mogućnosti (permutacija) na koji se ostvaruje raspodjela (*) $N_i \leftrightarrow E_i$ $\forall i$ od N čestica $N = \sum_i N_i$

1° $B_1 = \dfrac{N!}{N_1!\, N_2! \ldots}$ (permutacije s ponavljanjem)

broj različitih mogućnosti za (*) bez obzira za moguće razmještavanje N_i unutar E_i na kvantne ćelije

2° $B = \dfrac{N!}{N_1!\, N_2! \ldots} \cdot g_1^{N_1} \cdot g_2^{N_2} \ldots$ (varijacije s ponavljanjem)

N_i čestica (molek.) na g_i kvant. ćelija ali ne međusobno permutiranje čestica općenito $N_i \leq g_i$

(**) ⇒ $\forall$ čestica može u $\forall$ ćeliju ⇒ $\underbrace{g_i \cdot g_i \cdots g_i}_{N_i} = g_i^{N_i}$

ili označimo ćelije redom $a_1, a_2, \ldots a_k, \ldots a_{g_i}$ ⇒ N_i čestica razmještamo u njih čini varijacije s ponavljanjem $\overline{V}_{g_i}^{N_i} = g_i^{N_i}$

npr. sve čestice N_i u prvoj ćeliji: a_1

⇔ varij. s ponavljanjem $\underbrace{a_1, a_1, \ldots a_1}_{N_i}$

(**) Postojanje ćelija $\Delta p = h^3$ ne znači da u njoj ne može biti više molekula (čestica), (*) njeno značenje je u tome da te molekule ne možemo međusobno razlikovati (budući su njihovi konjugirani parovi koordinata $\Delta q_k \Delta p_k \simeq h$), dok molekule (čestice) u različitim ćelijama možemo međusobno razlikovati

(*) jedino Pauli-jev princip je iznimka

→ broj ćelija g_i u energ. intervalu $E_i = E^{(i)} - E^{(i-1)}$ dakle kažemo broj mogućnosti međusobnog razlikovanja istovrsnih čestica u tom energ. intervalu, pa i neki konačan broj različitih smještaja N_i čestica

→ u klasičnoj slici su energ. intervali E_i bili bi u tom pogledu (**) ekvivalentni, tj. bi za sve njih postojala neograničena mogućnost razlikovanja, kao i smještaja N_i čestica ⇒ $B = B_1$

originalno

→ ako je $g_i \gg N_i$ naslućujemo da će približno biti ispunjeno (**)

(bolje? $g_i \gg N$ $\forall i$)

→ za kojuKakvu raspodjelu $N_i \leftrightarrow E_i$ B ima maximum tj. koja raspodjela ima najveću statist. težinu

? broj raspodjela koje odg. istoj energ. mi?

→ varirano B po nivoima, tj. variranje čestica po nivoima

ograničenja kod variranja, tj. u variranju čestica nisu potpuno slobodni

$$N = \sum_i N_i \quad / \cdot \alpha \qquad U = \sum_i E_i N_i \quad / \beta$$ očuvanje energije

→ Max. tj. B metodom Lagrange multiplikatora: α, β

$$\delta N = 0 \quad / \cdot \alpha \qquad \delta U = 0 \quad / \beta \qquad \text{jer } N, U \text{ konst.}$$

za $B = \max \Rightarrow \ln B = \max \Rightarrow \delta \ln B = 0$ *)

opet uvjet za ekstrem,

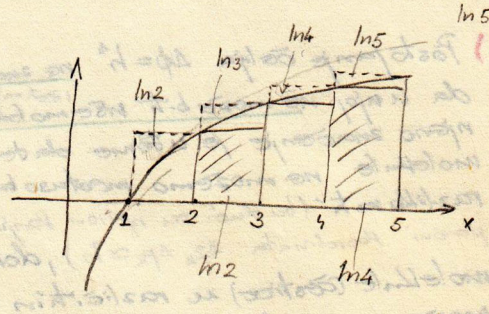
$$\Rightarrow \delta (\ln B - \alpha N - \beta U) = 0 \qquad (*)$$

δN_i - promjena broja molek. na E_i - tom nivou

(→ (**))

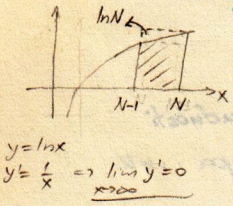
Stirling-ova formula

$$\ln N! = \ln 1 + \ln 2 + \ldots + \ln N$$
$$= 0 + 1 \cdot \ln 2 + 1 \cdot \ln 3 + \ldots + 1 \cdot \ln N$$



$$\ln 5! \geq \int_1^5 \ln x \, dx \qquad (**)$$

za $N \gg 1 \Rightarrow \ln N! \approx \int_1^N \ln x \, dx = (x \ln x - x)\Big|_1^N = N \ln N - N - 0 + 1 \overset{N \gg 1}{=} N \ln N - N$



$y = \ln x$, $y' = \frac{1}{x} \Rightarrow \lim_{x \to \infty} y' = 0$

$$\frac{\int_{N-1}^{N} \ln x \, dx}{\ln N} = \frac{\ln \frac{N^N}{e^{(N-1)N-1}}}{\ln N} \overset{N \gg 1}{=} \frac{\ln \frac{N^N}{e^{(N)N-1}}}{\ln N} = \frac{N \ln N - 1}{\ln N} \approx 1$$

$$= N(\ln N - 1) = N \ln \frac{N}{e} = \ln \left(\frac{N}{e}\right)^N$$

$$\Rightarrow N! \approx \left(\frac{N}{e}\right)^N \cdot \sqrt{2\pi N} \text{ za } N \gg 1$$

$$B = N! \prod_i \frac{g_i^{N_i}}{N_i!} = \frac{N^N}{e^N} \prod_i \frac{g_i^{N_i}}{\frac{N_i^{N_i}}{e^{N_i}}} = \frac{N^N}{e^N} \prod_i \frac{g_i^{N_i} \cdot e^{N_i}}{N_i^{N_i}} = \frac{N^N}{e^N} \cdot \underbrace{\prod_i e^{N_i}}_{e^{\sum N_i} = e^N} \cdot \prod_i \frac{g_i^{N_i}}{N_i^{N_i}}$$

$$B = N^N \cdot \prod_i \left(\frac{g_i}{N_i}\right)^{N_i} = N^N \prod_i \left(\frac{N_i}{g_i}\right)^{-N_i}$$

$$\ln B = N \ln N - \sum_i N_i \ln \frac{N_i}{g_i}$$

$N = \text{const} \quad 0 = \delta N = \delta \sum_i N_i = \sum_i \delta N_i \Rightarrow \sum_i \delta N_i = 0 \quad / \cdot \alpha$ (***)

$U = \text{const} \quad 0 = \delta U = \delta \sum_i N_i E_i = \sum_i E_i \delta N_i \Rightarrow \sum_i E_i \delta N_i = 0 \quad / \beta$

($E_i = \text{const}$ za varijacije po česticama)

*) $\Rightarrow \delta\left(N\ln N - \sum_i N_i \ln\frac{N_i}{g_i}\right) = 0$

$$\delta N\ln N = \sum_i \frac{\partial N\ln N}{\partial N_i}\delta N_i = \sum_i (\ln N+1)\delta N_i = (\ln N+1)\underbrace{\sum_i \delta N_i}_{=0} = 0$$

$$\delta\left(\sum_i N_i \ln\frac{N_i}{g_i}\right) = \sum_i \frac{\partial \sum_i N_i \ln\frac{N_i}{g_i}}{\partial N_i}\delta N_i = \sum_i \frac{\partial N_i \ln\frac{N_i}{g_i}}{\partial N_i}\delta N_i =$$

$$= \sum_i \left(\ln\frac{N_i}{g_i} + N_i \cdot \frac{1}{\frac{N_i}{g_i}}\cdot\frac{1}{g_i}\right)\delta N_i = \sum_i \left(\ln\frac{N_i}{g_i}+1\right)\delta N_i$$

$$\delta \ln B = -\sum_i \left(\ln\frac{N_i}{g_i}+1\right)\delta N_i$$

(*) $\Rightarrow$

$$-\sum_i \left(\ln\frac{N_i}{g_i} + 1 + \alpha + \beta E_i\right)\delta N_i = 0 \qquad (*)$$

original!!!

(**) možemo pisati u obliku $\sum_{i=1}^{n} a_{ki}\,\delta N_i = 0 \;/\cdot\lambda_k \quad k=1,2$ gdje je $a_{1i}=1 \;\forall i=1,\dots n$, $a_{2i}=E_i$

(*) možemo pisati u obliku

ako označimo $X_i = \ln\frac{N_i}{g_i} + 1$

$$\sum_{i=1}^{n}\left(X_i + \sum_{k=1}^{2}\lambda_k a_{ki}\right)\delta N_i = 0$$

$$\sum_{r=1}^{2}\left(X_r + \sum_{k=1}^{2}\lambda_k a_{kr}\right)\underbrace{\sum_{i=3}^{n}\gamma_{ir}\delta N_i}_{\delta N_r} + \sum_{i=3}^{n}\left(X_i + \sum_{k=1}^{2}\lambda_k a_{ki}\right)\delta N_i = 0$$

$$\sum_{i=3}^{n}\delta N_i\left[\sum_{r=1}^{2}\gamma_{ir}\left(X_r + \sum_{k=1}^{2}\lambda_k a_{kr}\right) + \left(X_i + \sum_{k=1}^{2}\lambda_k a_{ki}\right)\right] = 0$$

$\delta_{ip}\delta N_p$ od slobodnih $(n-2)$ varijacija odaberimo $\delta N_i = \delta_{ip}\delta N_p \quad p=3,\dots n$

$$\Rightarrow \sum_{r=1}^{2}\gamma_{pr}\left(X_r + \sum_{k=1}^{2}\lambda_k a_{kr}\right) + \left(X_p + \sum_{k=1}^{2}\lambda_k a_{kp}\right) = 0$$

$$\Rightarrow \sum_{k=1}^{2}\lambda_k a_{kr} = -X_r \quad r=1,2$$

zbog (*) & (**) Cramer-sistem $\exists!$ moguće odabrati $\lambda_k \quad k=1,2$

dakle da $\left(X_r + \sum_{k=1}^{2}\lambda_k a_{kr}\right) = 0 \quad r=1,2 \Rightarrow \left(X_p + \sum_{k=1}^{2}\lambda_k a_{kp}\right) = 0$ gdje u $\forall$ pojedinom slučaju $p=3,\dots n$

$$\Rightarrow \underbrace{X_i + \sum_{k=1}^{2}\lambda_k a_{ki} = 0}_{\alpha 1 + \beta E_i} \quad \forall i = 1,\dots n$$

$$\Rightarrow \ln\frac{N_i}{g_i} + 1 + \alpha + \beta E_i = 0 \quad \forall i = 1,\dots n$$

$$N_i = g_i \cdot e^{-1-\alpha-\beta E_i}$$ Boltzmann 1871

dakle najvjerojatnija raspodjela (β=max) $N_i = \text{const}\cdot e^{-\beta E_i}$

$\sum_{i=1}^{n} a_{ki}\,\delta N_i = 0$ sistem od 2 jednadžbe s n nepoznanica δN_i

$\text{rg}\left[(a_{ki})_{\substack{k=1,2\\ i=1,n}}\right] = 2$ (*)

$\Rightarrow \sum_{k=1}^{2}\lambda_k \sum_{i=1}^{n} a_{ki}\delta N_i = 0$ $\quad \lambda_1 = \alpha \quad \lambda_2 = \beta$

$\Rightarrow \sum_{i=1}^{n}\left(\sum_{k=1}^{2}\lambda_k a_{ki}\right)\delta N_i = 0$

odaberemo dakle numeraciju da je: (**)

$\sum_{i=1}^{2} a_{ki}\,\delta N_i = \underbrace{-\sum_{i=3}^{n} a_{ki}\delta N_i}_{\text{"}\beta_k} \quad k=1,2$ & $\text{rg}\left[(a_{ki})_{\substack{k=1,2\\ i=1,2}}\right] = 2$

$\exists!$ Cramer sistem

$r=1,2 \quad \delta N_r = \frac{\Pi_r}{\Pi} = \sum_{i=3}^{n}\gamma_{ir}\delta N_i$ (kodiramo po r-tom stupcu gdje su β_k-ovi)

$n-2$ slob. varijacija, a 2 zavisna od njih

Prijelaz :

Prelazimo se na pretpostavku da su energije kontinuirane veličine

$$\sum_i \;\; \begin{matrix}\text{po kvantiz.}\\ \text{energ. st.}\end{matrix} \;\; \rightarrow \int d\phi$$

integracijom po faznom prostoru

Kontinuirana promj. energ. u faznom prost.

Kvantiz. energija:

$$\text{Broj stanja} = g_1 + g_2 + \dots = \sum_i g_i$$

suma svih kvant. čelija po svim energ. nivoima (intervalima)

Kontinuirana energija:

$$\sum_{i=1}^{n} g_i \;\rightarrow\; \frac{\text{volum. } \phi \text{ prost.}}{\text{vol. fazne ćelije}} = \frac{\int d\phi}{\Delta\phi = h^s}$$

$\nearrow$ $n \to \infty \Rightarrow g_i \to 0$

$\Delta\phi_i$ volumen faznog prostora (u kojoj pripada interval energije

$$\frac{\Delta\phi_i}{\Delta\phi} = \frac{\Delta\phi_i}{h^s} \qquad E_i \;\; t_j: E^{(i)}, E^{(i)} + \Delta E^{(i)}$$

$\Rightarrow$ $g_i \rightarrow \frac{1}{h^s} d\phi$

broj ćelija u E_i intervalu — broj ćelija za $E, E+dE$

$E_i = (E^{(i)}, E^{(i)} + \Delta E^{(i)}) \rightarrow (E, E+dE)$

→ μ - prostoru s - st. slobode $\Delta\phi = h^s$

$$\sum_i g_i \rightarrow \frac{1}{h^s}\int d\phi = \int \frac{1}{h^s} d\phi$$

integral po cijelom μ prostoru

po svim energ. nivoima

$$N = \sum_i N_i = \sum_i g_i \, e^{-1-\alpha} \cdot e^{-\beta E_i} = e^{-1-\alpha} \sum_i g_i \, e^{-\beta E_i} \rightarrow e^{-1-\alpha} \int_{\mu\text{-prost.}} \frac{1}{h^s} d\phi \cdot e^{-\beta E}$$

$$\rightarrow e^{-1-\alpha} \int_{\mu\text{-prost.}} \frac{1}{h^s} e^{-\beta E} d\phi = e^{-1-\alpha} \cdot \frac{1}{h^s} \int_{\mu\text{-prost.}} e^{-\beta E} d\phi$$

$\Rightarrow$ odredimo α

$$\int_{\mu\text{-pr.}} dW = 1 \Leftrightarrow N = \int_{\mu\text{-prost.}} e^{-1-\alpha} \frac{1}{h^s} e^{-\beta E} d\phi \Rightarrow e^{1+\alpha} = \frac{1}{N h^s} \int_{\mu} e^{-\beta E} d\phi$$

jer $N_i = g_i \, e^{-1-\alpha} e^{-\beta E_i} \rightarrow dN = \frac{1}{h^s} d\phi \cdot e^{-1-\alpha} e^{-\beta E_i}$

$$\Rightarrow dN = e^{-1-\alpha} \frac{1}{h^s} e^{-\beta E} d\phi$$

$N_i \rightarrow dN$

broj čestica u E_i intervalu — broj čestica u $E, E+dE$

dN

$$dW = \frac{dN}{N} = e^{-1-\alpha} \cdot \frac{1}{h^s \cdot N} \cdot e^{-\beta E} d\phi$$

vjerojatnost da je neki broj molek. unutar $d\phi$ ovisi o $\infty d\phi$ što odgovara Liouv. th.

$$dW = g(E)\, d\phi$$

- vjerojatnost da se molek. nalazi u tom intervalu $d\phi$

$$\Rightarrow \quad g(E) = e^{-1-\alpha} \cdot \frac{1}{N \cdot h^s} e^{-\beta E}$$

Boltzmannova raspodjela

za termički uravnotežan sistem

N, V, T

$$\Rightarrow \quad g(E) = \frac{e^{-\beta E}}{\int_{\mu} e^{-\beta E} d\phi}$$

(1)

$$\frac{3}{2}kT = \bar{E} = \frac{\int_{\mathcal{C}} E e^{-\beta E}\, d\phi}{\int_{\mathcal{C}} e^{-\beta E}\, d\phi} = \frac{3}{2}\cdot\frac{1}{\beta} \Rightarrow \boxed{\beta = \frac{1}{kT}}$$

$$E = \frac{p^2}{2m} + E_p \qquad E_p = \begin{cases} 0 & \text{unutar} \\ \infty & \text{izvan posude} \end{cases}$$

(2)

$$\bar{E} = \frac{\iiint_V \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{p_x^2+p_y^2+p_z^2}{2m} e^{-\frac{\beta}{2m}(p_x^2+p_y^2+p_z^2)}\, dx\,dy\,dz\,dp_x\,dp_y\,dp_z}{\iiint_V \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} e^{-\frac{\beta}{2m}(p_x^2+p_y^2+p_z^2)}\, dx\,dy\,dz\,dp_x\,dp_y\,dp_z}$$

$$\bar{E} = \frac{V\frac{1}{\beta}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \beta\frac{(p_x^2+p_y^2+p_z^2)}{2m} e^{-\frac{\beta}{2m}(p_x^2+p_y^2+p_z^2)}\, dp_x\,dp_y\,dp_z}{V\cdot\left(\int_{-\infty}^{\infty} e^{-\frac{\beta}{2m}p_x^2}\, dp_x\right)^3}$$

$$\left(\frac{2\pi m}{\beta}\right)^{3/2}$$

$$t = \sqrt{\frac{\beta}{2m}}\,p_x \qquad r = \sqrt{\frac{\beta}{2m}}\cdot p_y \qquad s = \sqrt{\frac{\beta}{2m}}\,p_z$$

$$\bar{E} = \frac{1}{\beta}\cdot\left(\frac{2\pi m}{\beta}\right)^{-3/2}\cdot\left(\frac{2m}{\beta}\right)^{3/2}\cdot\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}(t^2+r^2+s^2)e^{-(t^2+r^2+s^2)}\, dt\,dr\,ds$$

$$\bar{E} = \frac{1}{\beta}\cdot\pi^{-3/2}\cdot\int_{-\infty}^{\infty}dt\int_{-\infty}^{\infty}dr\int_{-\infty}^{\infty}(t^2+r^2+s^2)e^{-(t^2+r^2+s^2)}\, ds$$

preko $t = u\sin\theta\cos\varphi$ $\quad r = u\sin\theta\sin\varphi$ $\quad s = u\cos\theta$

& Jakobijana $\Rightarrow$

$$4\pi\int_0^{\infty} u^2 e^{-u^2}\cdot u^2\, du = 4\pi\int_0^{\infty} u^4 e^{-u^2}\, du$$

$$= 2\pi\int_{-\infty}^{\infty} u^4 e^{-u^2}\, du =$$

$$= 2\pi\cdot\frac{4-1}{2}\cdot\frac{2-1}{2}\cdot\sqrt{\pi} = \frac{3}{2}\pi^{3/2}$$

$$\Rightarrow \bar{E} = \frac{1}{\beta}\pi^{-3/2}\cdot\frac{3}{2}\pi^{3/2} = \frac{3}{2\beta}$$

$$\frac{3}{2}kT = \bar{E} = \frac{\int_\Gamma E e^{-\beta E}\, d\phi}{\int_\Gamma e^{-\beta E}\, d\phi}$$

- neovisi o V, jer se on kratiti

$\Downarrow$

- vodimo V ili je s njim vezan

$$\int_\Gamma E e^{-\beta E}\, d\phi \overset{(*)}{=} -\left(\frac{\partial}{\partial \beta} \int_\Gamma e^{-\beta E}\, d\phi\right)_V$$

(*) da li se smije derivirati, jer $\int_\Gamma$ obično neproprio integral

$$\bar{E} = -\left[\frac{\partial}{\partial \beta} \ln\left(\int_\Gamma E e^{-\beta E}\, d\phi\right)\right]_V$$

$$\bar{E} = -\left[\frac{\partial}{\partial \beta} \cdot \ln\left((2\pi m)^{3/2} \cdot \beta^{-3/2}\right)\right]_V$$

$$\bar{E} = -\left[\frac{\partial}{\partial \beta}\left(\ln V + \frac{3}{2}\ln 2\pi m - \frac{3}{2}\ln\beta\right)\right]_V$$

$$= -\left[\frac{1}{V}\cdot\underbrace{\frac{\partial V}{\partial \beta}}_{0} + 0 - \frac{3}{2}\cdot\frac{1}{\beta}\right]$$

$$\left.\begin{aligned} \bar{E} &= \frac{3}{2}\cdot\frac{1}{\beta} \\ \bar{E} &= \frac{3}{2}kT \end{aligned}\right\} \Rightarrow \underline{\beta = \frac{1}{kT}}$$

h - se ne smije populjivati u klas. izrazu (kontinuirana varij.)

$$dW = \frac{dN}{N} = \frac{e^{-1-\alpha}\cdot\frac{1}{h^s}e^{-\beta E}d\phi}{\int_{\mu\text{-prost.}} e^{-1-\alpha}\cdot\frac{1}{h^s}e^{-\beta E}d\phi}$$

$$\Leftrightarrow 1 = \int_\mu dW = e^{-1-\alpha}\frac{1}{h^s N}\int_\mu e^{-\beta E}d\phi$$

$$\Rightarrow e^{-1-\alpha}\cdot\frac{1}{h^s N} = \frac{1}{\int_\mu e^{-\beta E}d\phi}$$

$$\boxed{dW = \frac{e^{-\beta E}d\phi}{\int_{\mu\text{-pr.}} e^{-\beta E}d\phi}}$$

α, β računamo iz uvjeta preko kojih smo ih uveli: α - konst. broja čestica

β - jednoatomnosti

Boltzmann-ova rasp. $\longrightarrow$ Maxwell-ova

za 1-at. idealni plin $\Rightarrow \beta = \frac{1}{kT}$ dolazano na papiru ①'

srednja vrijednost fiz. veličine $G(q,p)$ $\quad q \equiv (q_1 \dots q^s)$, $p \equiv (p_1 \dots p^s)$

$dW = g(E)d\phi = g(E,p)d\phi$

$$\bar{G} = \int_\mu G(q,p)\,dW = \frac{\int G(q,p)e^{-\beta E(q,p)}d\phi}{\int_\mu e^{-\beta E(q,p)}d\phi}$$

!!! odnos pro

Primjer: 1-A idealni plin izvan djelovanja vanjskih sila $\Rightarrow s = 3$

↓ne 3 indentična čestica

$$N = \int_\mu e^{-1-\alpha}\frac{1}{h^s}e^{-\beta E}d\phi$$

$$\Rightarrow e^{1+\alpha} = \frac{1}{Nh^3}\iiint_{-\infty}^{\infty} e^{-\beta E}\,dx\,dy\,dz\,dp_x\,dp_y\,dp_z$$

$E = \frac{p^2}{2m} + E_p \qquad p^2 = \sum p_x^2$

$$E_p = \begin{cases} 0 & \text{u posudi zatvorenoj volumena } V \\ \infty & \text{na granici i izvan posude} \end{cases}$$

$e^{-\frac{E_p}{kT}}$ $\quad \iiint dx\,dy\,dz$ se svodi samo na integraciju stanje posude V

$$e^{1+\alpha} = \frac{V}{Nh^3}\left(\int_{-\infty}^{\infty} e^{-\beta\cdot\frac{p_x^2}{m}}dp_x\right)^3$$

za $e^{-\beta E} = e^{-\infty} = 0$

$$e^{1+\alpha} = \frac{V}{Nh^3}\left(\int_{-\infty}^{\infty} e^{-\frac{\beta}{2m}p_x^2}\,dp_x\right)^3 \qquad t=\sqrt{\frac{\beta}{2m}}\,p_x \Rightarrow e^{1+\alpha} = \frac{V}{Nh^3}\left(\frac{2m}{\beta}\right)^{3/2}\left(\int_{-\infty}^{\infty} e^{-t^2}dt\right)^3$$

$$(\sqrt{\pi})^3$$

$$e^{1+\alpha} = \frac{V}{Nh^3}\cdot\left(\frac{2\pi m}{\beta}\right)^{3/2} \qquad \beta = \frac{1}{kT}$$ razveo na papiru za L-A plin, idealni

lako nadamo α

$$e^{1+\alpha} = \frac{V}{Nh^3}\left(2\pi m kT\right)^{3/2}$$

Maxwell. raspodjela iz Boltzmann-ove $dW = g(E)\cdot V\cdot dp^3$ $\quad dW = g(v)\cdot d^3V$

$$\Rightarrow g(E) = \frac{1}{V}(2\pi m kT)^{-3/2}\cdot e^{-\frac{E}{kT}} \qquad \frac{g(E)}{g(v)} = \frac{1}{V\cdot m^3}$$

$$= \frac{1}{V\cdot m^3}\underbrace{\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{E}{kT}}}_{g(v)} \text{ per } \vec{v}, \vec{v}+d^3V$$

$$\frac{N_i}{g_i} = e^{-1-\alpha}\cdot e^{-\beta E_i}$$

$$\rightarrow \frac{N_i}{g_i} = \underbrace{\frac{Nh^3}{V(2\pi m kT)^{3/2}}}_{=k}\cdot e^{-\frac{E_i}{kT}}$$

napučenost

populacija i-tog energ. nivoa

$k \ll 1$ uvjet primjenjivosti klas. statističke fizike $\Leftrightarrow$ $N_i \ll g_i$ mala napučenost energ. nivoa

$E_i \geq 0$ za sve energ. nivoe

$E_{i+1} > E_i$ $\quad$ 1° na T $\quad \frac{N_i}{g_i}$ napučenost E_i-nivoa

2° na T' $\quad \frac{N_{i+1}}{g_{i+1}}$ napučenost E_{i+1}-nivoa

zahtjev $\frac{N_i}{g_i} = \frac{N_{i+1}}{g_{i+1}} \Rightarrow T^{-\frac{3}{2}} e^{-\frac{E_i}{kT}} = T'^{-\frac{3}{2}} e^{-\frac{E_{i+1}}{kT'}} \Rightarrow \left(\frac{T'}{T}\right)^{3/2} = e^{+\frac{1}{k}\left(\frac{E_i}{T}-\frac{E_{i+1}}{T'}\right)}$

$T' > T \Rightarrow \frac{E_i}{T} - \frac{E_{i+1}}{T'} > 0 \Rightarrow \frac{T'}{T} > \frac{E_{i+1}}{E_i} > 1$

ORIGINALNO!!!

ili:

$\rightarrow$ na papiru $E_{i+1} > E_i \Rightarrow (T_{max})_{i+1} > (T_{max})_i$ (*)

- porastom T populacija svih energ. nivoa raste, tj. prema (*) temperatura za koju je populacija nekog E_i-tog energ. nivoa maksimalna, mora biti to viša što je taj energ. nivo viši.

$T>0$ $\qquad$ $T=0$ $\qquad$ $E_1=0$

na papiru:

$$\lim_{T\to 0}\left(\frac{N_i}{g_i}\right) = \begin{cases} 0 & E_i > 0 \\ \neq 0 & E_i = 0 \end{cases}$$

Primjer: He $\quad T = 300\,K \quad \frac{N}{V} = 2{,}68\cdot 10^{+19}\,cm^{-3} \quad m = 6{,}68\cdot 10^{-24}\,g$ $\quad K = \frac{R}{A}$

$$E_1 = 0 \Rightarrow \frac{N_1}{g_1} \approx 3{,}3\cdot 10^{-6} \qquad \approx 3\cdot 10^{19}\,cm^{-3}\cdot\frac{(6\cdot 10^{-27})^3\cdot erg^3 s^3}{(6\cdot 7\cdot 10^{-24}\cdot 1{,}38\cdot 10^{-16}\cdot 3\cdot 10^2)^{3/2}\,(g\cdot erg)^{3/2}} = g^3 cm^{-3} s^{-3}$$

$$(g^2 cm^2 s^{-2})^{3/2}$$

tek na milijun stanja čestica je u E_1 nivou, tj. na normal. dnevnoj naseljenost osnovnog kvantnog stanja je izrazito mala

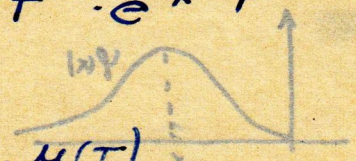
$\Rightarrow$ mora biti $g_i \gg 1$ da bi taj rezultat bio korektno izveden! (da smo smjeli upotrijebiti Stirlingovu formulu)

dobila ima smisla ako je $N_1 > 1$

it never rains in south California - Suzy

$$\frac{N_i}{g_i} = \frac{Nh^3}{V(2\pi mk)^{3/2}} \cdot T^{-3/2} \cdot e^{-\frac{E_i}{k}\cdot\frac{1}{T}}$$

populacija i-tog energ. nivoa E_i



$$= \frac{Nh^3}{V(2\pi mk)^{3/2}} \cdot y(T)$$

$$y(T) = \left(\frac{1}{T}\right)^{3/2} \cdot e^{-\alpha_i \cdot \frac{1}{T}} \qquad \alpha_i = \frac{E_i}{k} \geq 0$$

$$T = \frac{1}{x}$$

$$\varphi(x) = y\left(\frac{1}{x}\right) = x^{3/2} \cdot e^{-\alpha_i x}$$

$$\boxed{\varphi(x) = x^{3/2} \cdot e^{-\alpha_i x} = \frac{x^{3/2}}{e^{\alpha_i x}}}$$

$$\lim_{T\to\infty} y(T) = \lim_{x\to 0} \varphi(x) = 0$$

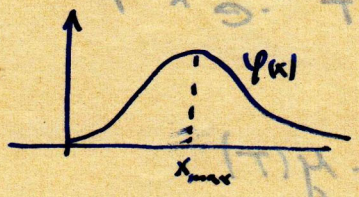
$$\lim_{T\to 0} y(T) = \lim_{x\to\infty} \varphi(x) = \lim_{x\to\infty} \frac{\frac{3}{2}\cdot\frac{1}{2}\cdot x^{-1/2}}{\alpha_i^2 e^{\alpha_i x}} =$$

$$= \lim_{x\to\infty} \frac{3}{4\alpha_i^2} \cdot \frac{1}{x^{1/2} e^{\alpha_i x}} = \begin{cases} 0 & \alpha_i > 0 \\ \neq 0 & \alpha_i = 0 \end{cases}$$

$\Rightarrow$ za $T=0$ $\frac{N_i}{g_i} \neq 0$ jedino za $E_i = 0$

Sve čestice se nalaze u najnižem energ. nivou

$\frac{N_i}{g_i} = max$ za $\varphi(x) = max$



$\varphi'(x) = \frac{3}{2} x^{1/2} e^{-a_i x} + x^{3/2}(-a_i) e^{-a_i x} = 0$

$x = \frac{3}{2a_i}$ $\quad T = \frac{1}{x} = \frac{2a_i}{3} = \frac{2}{3}\frac{E_i}{K}$

$\Rightarrow$ za odredeni E_i - nivo populacija $\frac{N_i}{g_i}$ je max. za temp. $(T_{max})_i = \frac{2}{3}\frac{E_i}{K}$

$\Rightarrow$ za $E_{i+1} > E_i \Rightarrow (T_{max})_{i+1} > (T_{max})_i$

$$k = \frac{N h^3}{V (2\pi m kT)^{3/2}}$$

$$\bar{p} \approx \sqrt{\bar{p}^2} = \sqrt{2mE} = \sqrt{2m \cdot \tfrac{3}{2} kT} = \sqrt{3mkT}$$

$$\frac{V}{N} \cdot (\sqrt{3mkT})^3 \gg h^3$$

Primjena Klas. statistike

$k \ll 1 \Leftrightarrow N_i \ll g_i$, tj. $\frac{N_i}{g_i} = k \cdot e^{-\frac{E_i}{kT}}$

$g_i \gg N_i$ ako broj kvant. stanja jako premašuje broj čestica na tom energ. nivou

$\Leftrightarrow$ napučenost kvantnih ćelija mala, dakle se kvant. statist. $\rightarrow$ klas. statistika ($g_i \gg N_i$)

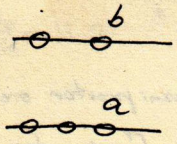
tj.:

$\Delta x \cdot \Delta p = h$ ako čestice padnu u istu kvantnu ćeliju ne možemo ih razlikovati

tj. ako je napučenost mala vjerojatnije je da će čestice pasti u različita kvantna ćelija, pa ćemo ih moći razlikovati, dakle da kvantna ćelija (osobina) neće moći do izražaja

$\rightarrow$ neće $\prod$ faktori $g_1^{N_1} \cdot g_2^{N_2} \cdots$

tj. neće doći do izražaja razlučivi razmještaji (mogućnosti) unutar E_i na ćelije, već će biti samo važno !!! koja će č. na E_i, dakle E_i neće se razlikovati ← međusobno po posebnosti.



U klas. razlikujemo a od b (godinile čestice)

U kvant. ne $\rightarrow$ nova statistika

primanja čestica zbog postojanja diskret. kvant. ćelija

vjerojatnosna korekcija u faktoru $\frac{N!}{N_1! N_2! \cdots}$

Suprotno IV 334.

Prosječna vrijednost energije

$$\bar{G}_{(q,p)} = \frac{\int_{(\mu)} G_{(q,p)} e^{-\beta E_{(q,p)}} d\phi}{\int_{(\mu)} e^{-\beta E_{(q,p)}} d\phi}$$

(μ-prost. dim = 2s st. slobode molek.

za 1 česticu $\bar{E}_{(q,p)} = \frac{\int_{(\mu)} E_{(q,p)} e^{-\beta E_{(q,p)}} d\phi}{\int_{(\mu)} e^{-\beta E_{(q,p)}} d\phi}$

$$\int_{(\mu)} E e^{-\beta E} d\phi = -\left(\frac{\partial}{\partial \beta} \int_{(\mu)} e^{-\beta E_{(q,p)}} d\phi \right)_V$$

$$\bar{E} = -\left[\frac{\partial}{\partial \beta} \ln \left(\int_{(\mu)} e^{-\beta E_{(q,p)}} d\phi \right) \right]_V =$$

$$= -\left[\frac{\partial}{\partial \beta} \ln \left(\frac{1}{h^s} \int_{(\mu)} e^{-\beta E} d\phi \right) \right]_V$$

uz konstantan volumen

par integral $\int_{(\mu)}$ vodi na volumen ili je povezan s volumenom

napomena! Markuševič (178-190) §289 deriviranje nepravog integrala po parametru samo ako je polučilo konvrg. i ako mu granice ne ovise o tom parametru

$$\Rightarrow \quad \bar{E} = -\left(\frac{\partial}{\partial \beta} \ln Z \right)_V \qquad Z = \frac{1}{h^s} \int_{(\mu)} e^{-\beta E_{(q,p)}} d\phi$$

fja. particije jedne čestice

$d\phi$ je dim $= h^s \Rightarrow$

$\Rightarrow Z$ je bez dimenzije

Ukupna energija cjelog plina:

$$U = \sum_i E_i \cdot N_i \equiv \sum_{k=1}^{N} E_k$$

$\sum_i$ sumacija po diskretnim energ. nivoima $E_i \equiv (E^{(i)}, E^{(i)} + \Delta E^{(i)})$

za $\sum_i \to \int_\mu d\phi$ $\Rightarrow$ $E_i \to E, E+dE$ $\quad N_i \to dN = e^{-1-\alpha} \cdot \frac{1}{h^3} e^{-\beta E} d\phi = N \cdot \frac{e^{-\beta E} d\phi}{\int_\mu e^{-\beta E} d\phi}$

original!!!

$$\Rightarrow \sum_i E_i N_i \to \int_\mu E\, dN = \int_\mu E \cdot N \cdot \frac{e^{-\beta E} d\phi}{\int_\mu e^{-\beta E} d\phi} = N \cdot \frac{\int_\mu E e^{-\beta E} d\phi}{\int_\mu e^{-\beta E} d\phi} = N\bar{E}$$

$N\left\{-\left[\frac{\partial}{\partial\beta} \ln z\right]_V\right\}$

$$\Rightarrow U = N\bar{E} = -\left[\frac{\partial}{\partial\beta} N \cdot \ln z\right]_V = -\left(\frac{\partial}{\partial\beta} \ln z^N\right)_V \qquad N = \sum_i N_i$$

za diskontinuir: $U = \sum_i N_i E_i \Rightarrow \frac{U}{N} = \sum_i E_i \frac{N_i}{N} = \sum_i E_i W_i = \bar{E} = \frac{\sum E_i g_i e^{-\beta E_i}}{\sum g_i e^{-\beta E_i}} = -\frac{d}{d\beta} \ln \left(\sum_i g_i e^{-\beta E_i}\right) \Big| \; Z = z^N$

$\Rightarrow U = -\frac{d}{d\beta} \ln z^N = -\frac{d}{d\beta} \ln Z$

Fja. particije cijelog sistema (od N čestica)

$$Z = \frac{1}{h^{3N}} \int_\Gamma e^{-\beta(E_1 + E_2 + \dots)} d\phi_1 d\phi_2 \dots d\phi_N$$

($\sum_{k=1}^{N} E_k$, $\prod_{k=1}^{N} d\phi_k$)

statistička suma $\to$ integral statistički

Fazni prostor sistema od N čest.

Γ - prostor dim. $2sN$

sN - stupnji slobode

s - stupanj slobode 1 čestice

E_k - energija k-te čestice

$d\phi_k$ - dif. volumni element

μ - prost. k-te molekule

$$Z = \frac{1}{h^{3N}} \int_\Gamma \prod_{k=1}^{N} e^{-\beta E_k} d\phi_k \qquad d\phi_k = d\Sigma_k\, dp_k = dq_{1_k} \dots dq_{s_k}\, dp_{1_k} \dots dp_{s_k}$$

→ čestice bez korelacije ($H = \sum_{k=1}^{N} H_k$) $\Rightarrow E_k(q_k, p_k) \quad \forall k = 1, \dots N$

$$\Rightarrow Z = \frac{1}{h^{3N}} \cdot \int_{\mu_1} e^{-\beta E_1} d\phi_1 \int_{\mu_2} e^{-\beta E_2} d\phi_2 \dots \int_{\mu_N} e^{-\beta E_N} d\phi_N = \frac{1}{h^{3N}} \cdot \prod_{k=1}^{N} \int_{\mu_k} e^{-\beta E_k(q_k, p_k)} d\phi_k$$

identične čestice bez korelacije $\Rightarrow E_k(q_k, p_k)$ isto za sve čestice $\Rightarrow \left(\int_{\mu_k} e^{-\beta E_k} d\phi_k\right)^N$

$$\Rightarrow Z = \left(\frac{1}{h^3} \int_{\mu_k} e^{-\beta E_k(q_k, p_k)} d\phi_k\right)^N = z^N$$

bilo koji $k = 1, \dots N$

$$\Rightarrow U = -\left(\frac{\partial}{\partial\beta} \ln Z\right)_V$$

$N = \sum_i N_i$

$U = \sum_i N_i E_i = N \cdot \bar{E} = -\frac{d}{d\beta} \ln Z$

$Z = z^N \qquad z = \sum_i g_i e^{-\beta E_i}$

$T = \frac{1}{k\beta}$

$\frac{\partial T}{\partial \beta} = -\frac{1}{k}\cdot\frac{1}{\beta^2} = -\frac{1}{k}\cdot k^2T^2 = -kT^2$

$\beta = \frac{1}{kT} \Rightarrow \frac{\partial}{\partial \beta} = -kT^2\frac{\partial}{\partial T}$

$\frac{\partial \phi}{\partial \beta} = \frac{\partial \phi}{\partial T}\cdot\frac{\partial T}{\partial \beta}$

(*) $U = kT^2\left(\frac{\partial}{\partial T}\ln Z\right)_V = T\left[\left(\frac{\partial}{\partial T}kT\ln Z\right)_V - k\ln Z\right] =$ $\quad T\left(kT\frac{\partial}{\partial T}\ln Z\right)_V$

$= -kT\ln Z + T\left(\frac{\partial}{\partial T}kT\ln Z\right)_V$ ovo je statistička fizika

Odgovarajuće relacije iz termodinamike:

$dF = -PdV - SdT$

$F = U - TS$, $S = -\left(\frac{\partial F}{\partial T}\right)_V$ $\Rightarrow F = U + T\left(\frac{\partial F}{\partial T}\right)_V \Rightarrow U = F - T\left(\frac{\partial F}{\partial T}\right)_V$ (**)

(*) & (**) iste strukture, komparacijom $\Rightarrow$

$Z = z^N$

slobodna energija sistema

$$F = -kT\ln Z$$

$S = -\left(\frac{\partial F}{\partial T}\right)_V = k\left(\frac{\partial}{\partial T}T\ln Z\right)_V$

Kvak u povezanosti stat. velič. i termodin. veličina

Boltzmann-ova relacija

→ u klasičnoj mehanici dozvoljena je inverzija vremena $t \to -t$

→ termodin. ne raspolaže s dovoljnim brojem informacija, ne zalazi u individualnost odnosi se na mnoštvo molekula

→ makro ista stanja postižu se na mnogo načina tj. velik broj mogućnosti da isto termodinam. veličina ima ista vrijednost - za različite rasporede u energ. nivoima

Količina(≠)mikrostruktura opisuje neko(=)makroskopsko stanje

početna vrijednost veličine M — konačna vrijednost velič. M.

$M_p(m_i) \to M_k(m_i')$ = konačno makroskopsko stanje

poč. broj mikrostanja — kon. broj mikrostanja koji realiziraju do kon. makrost. stanje M_k

$\neq$ jer $m_i \neq m_i'$ tj. i različ. vjerojatnost za poč. i kon. stanje

$m_i' \gg m_i$ $\Rightarrow$ vjerojatnost konačnog stanja mnogo veća

(**)

→ broj mikrostanja je jednak

$$\mathcal{B} = \frac{N!}{N_1! N_2! \ldots} g_1^{N_1} \cdot g_2^{N_2} \ldots$$

= ukupan broj mikrostanja koje ostvaruju dano makrostanje

$\mathcal{B}$ definiramo kao **termodin. vjerojatnost** za ostvarenje danog makrostanja

općenito $\mathcal{B} \gg 1$ dok matem vjerojatnost $W = \frac{k}{m} \leq 1$

→ broj načina jedini kriterij za vjerojatnost (apriorna vjerojatnost)

$S(E)$ ← još i ha. ka. (odbir. mol. u.)

→ sistem prelazi u termodin. vjerojatnija stanja (teži u stanja veće S)

dva sistema: $d'Q = 0 \Rightarrow dS \geq 0$

(1)	(2)	
$S_1(\mathcal{B}_1)$	$S_2(\mathcal{B}_2)$	entropija
$\mathcal{B}_1$	$\mathcal{B}_2$	vjerojatnost

u mislima spojimo ta dva sistema (bez interakcije)

⇒ nezavisni sistemi = nezavisni događaji:

entropija aditivna veličina $S = S_1 + S_2$ $\qquad \mathcal{B} = \mathcal{B}_1 \cdot \mathcal{B}_2$

$$\Rightarrow \quad S(\mathcal{B}_1 \mathcal{B}_2) = S_1(\mathcal{B}_1) + S_2(\mathcal{B}_2) \quad / \cdot \mathcal{B}_1 \frac{\partial}{\partial \mathcal{B}_1}$$

$$\mathcal{B}_1 \frac{\partial}{\partial \mathcal{B}_1} S(\mathcal{B}) = \mathcal{B}_1 \frac{dS_1}{d\mathcal{B}_1}$$

$$\underbrace{\mathcal{B}_1 \cdot \mathcal{B}_2}_{\mathcal{B}} \frac{\partial S(\mathcal{B})}{\partial \mathcal{B}} = \mathcal{B}_1 \frac{dS_1}{d\mathcal{B}_1}$$

$\mathcal{B} = \mathcal{B}_1 \cdot \mathcal{B}_2$

budući: $\frac{\partial S(\mathcal{B})}{\partial \mathcal{B}_1} = \frac{\partial S(\mathcal{B})}{\partial \mathcal{B}} \frac{\partial \mathcal{B}}{\partial \mathcal{B}_1} = \mathcal{B}_2 \cdot \frac{\partial S(\mathcal{B})}{\partial \mathcal{B}}$

$$\mathcal{B} \frac{dS}{d\mathcal{B}} = \mathcal{B}_1 \frac{dS_1}{d\mathcal{B}_1} = \mathcal{B}_2 \frac{dS_2}{d\mathcal{B}_2} = \text{konst.}$$

$$\Rightarrow \quad dS = k \cdot \frac{d\mathcal{B}}{\mathcal{B}} \quad \Rightarrow \quad S = k \cdot \ln \mathcal{B} + \alpha$$

stavimo $\alpha = 0$ jer je S definir. do na adit. konst.

$$\boxed{S = k \cdot \ln \mathcal{B}}$$

iz druge relacije dobiva se: $k = K = 1{,}38 \cdot 10^{-16}$ $\frac{\text{ergs}}{\text{st}^{-1}}$

iz (**)

orig!

$$\left.\begin{aligned}\sum_i \delta N_i &= 0\\ \sum_i E_i \delta N_i &= 0\end{aligned}\right\}$$ možemo pisati u obliku

$$\sum_{i=1}^{m} a_{ki}\,\delta N_i = 0 \;/\cdot\lambda_k \quad k=1,2 \quad \text{gdje} \quad a_{1i}=1 \quad \forall i=1,\dots m \qquad a_{2i}=E_i$$

& pretp. $\operatorname{rang}\left[(a_{ki})_{ki}\right]_{(2,m)} = 2$ $\qquad \lambda_1 = -\alpha \quad \lambda_2 = -\beta$

$$\Rightarrow \sum_{k=1}^{2}\lambda_k \sum_{i=1}^{m} a_{ki}\,\delta N_i = 0$$

$$\sum_i \left[\ln\frac{g_i - N_i}{N_i} - \alpha - \beta E_i\right]\delta N_i = 0$$ možemo pisati (ako označimo $X_i = \ln\frac{g_i - N_i}{N_i}$) u obliku

$$\sum_{i=1}^{m}\left(X_i + \sum_{k=1}^{2}\lambda_k a_{ki}\right)\delta N_i = 0$$

→ odaberemo takvu numeraciju (indeksa) da je $\sum_{i=1}^{2} a_{ki}\,\delta N_i = \underbrace{-\sum_{i=3}^{m} a_{ki}\,\delta N_i}_{=\beta_k} \quad k=1,2$

& $\operatorname{rang}\left[(a_{ki})_{ki}\right]_{(2,2)} = 2$ } tj. Cramerov sustav (✡)

$$\Rightarrow \quad r=1,2 \quad \delta N_r = \frac{D_r}{D} = \sum_{i=3}^{m}\gamma_{ir}\,\delta N_i$$

(m-2 slobodnih varijacija, a 2 zavisne od njih)

$$\Rightarrow \sum_{r=1}^{2}\left(X_r + \sum_{k=1}^{2}\lambda_k a_{kr}\right)\sum_{i=3}^{m}\gamma_{ir}\,\delta N_i + \sum_{i=3}^{m}\left(X_i + \sum_{k=1}^{2}\lambda_k a_{ki}\right)\delta N_i = 0$$

$$\sum_{i=3}^{m}\delta N_i\left[\sum_{r=1}^{2}\gamma_{ir}\left(X_r + \sum_{k=1}^{2}\lambda_k a_{kr}\right) + \left(X_i + \sum_{k=1}^{2}\lambda_k a_{ki}\right)\right] = 0$$

od slobodnih (m-2) varijacija odaberimo $\delta N_i = \delta_{ip}\,\delta N_p \quad p=3,\dots m$

$$\Rightarrow \sum_{r=1}^{2}\gamma_{ip}\left(X_r + \sum_{k=1}^{2}\lambda_k a_{kr}\right) + \left(X_p + \sum_{k=1}^{2}\lambda_k a_{kp}\right) = 0$$

zbog (✡) moguće je odabrati λ_k $k=1,2$ tako da je $X_r + \sum_{k=1}^{2}\lambda_k a_{kr} = 0 \quad r=1,2$

$$\Rightarrow \quad X_p + \sum_{k=1}^{2}\lambda_k a_{kp} = 0 \qquad p=3,\dots m$$

$$\Rightarrow \quad \underline{X_i + \sum_{k=1}^{2}\lambda_k a_{ki} = 0} \qquad \underline{\forall i = 1,\dots m}$$

$$\delta(\ln B - \alpha N - \beta U) = 0$$

$$g_i = \frac{N_i}{g_i} = \frac{1}{e^{\alpha + \beta \bar{E}_i} + 1}$$

$$\left.\begin{aligned} S &= S_1 + S_2 \\ B &= B_1 B_2 \Rightarrow \ln B = \ln B_1 + \ln B_2 \end{aligned}\right\} \Rightarrow S = k \cdot \ln B$$

II z.t.d. $dS \geq \frac{d'Q}{T}$ za $d'Q \Rightarrow dS \geq 0$ tj. da sistem teži u stanje gdje je S veći.

- vrijedi u prosjeku, uzmši u fluktuacije

dakle ne vrijedi egzaktno, općenito

$$B = e^{\frac{S}{k}} \qquad B_m = e^{\frac{S_m}{k}}$$

max. vjerojatnost $\Rightarrow S_m$ entropija termičke ravnoteže

$$\Rightarrow \frac{B}{B_m} = e^{-\frac{\Delta S}{k}} \leq 1 \qquad 0 \leq \Delta S = S_m - S$$

Fluktuacije oko ravnotežnog stanja su ako je $\Delta S \lesssim k$

$$\Rightarrow \frac{\Delta S}{k} \lesssim 1 \Rightarrow e^{\frac{\Delta S}{k}} \lesssim e \Rightarrow e^{-\frac{\Delta S}{k}} \gtrsim e^{-1} \Rightarrow \frac{B}{B_m} \gtrsim \frac{1}{e} \approx \frac{1}{2}$$

tj. fluktuacije su ako $1 \geq \frac{B}{B_m} \geq \frac{1}{e}$ $\Rightarrow e^{-\frac{\Delta S}{k}} \geq e^{-1} \Rightarrow 1 \geq \frac{\Delta S}{k} \Rightarrow \Delta S \leq k$

(*) originalno!!! & Supek 118

$$B = \frac{N!}{N_1! N_2! \ldots} q_1^{N_1} \cdot q_2^{N_2} \ldots$$ vjerojatnost raspodjele N čestica na E_i - intervale i unutar njih na ćelije

$$B = N^N \cdot \prod_i \left(\frac{q_i}{N_i}\right)^{N_i}$$

→ Zamislimo da mjerimo stanje plina grijanjem. Ako taj proces dobro poklapamo, plin prolazi kroz sama stanja ravnoteže, pa njegova raspodjela u T čaru mora biti Kanonska

(*) $N_i = q_i e^{-1-\alpha-\beta E_i}$

Kad tijelu privodimo toplinu, tad se molekule premještaju prema višim energ. nivoima. Energije čine ustvari kontinuum (klas. statistika), pa se ugrijavanjem molekule kontinuirano pomiču prema višim energijama.

Diskretnost je tu uzeta zato, da olakša pregled (i to je bitna razlika prema kvantnoj teoriji, gdje taj zaključak ne bi vrijedio).

$$\ln B = N \ln N - \sum_i N_i \ln \frac{N_i}{q_i} \qquad N = \sum_i N_i = \text{const.} \Rightarrow \sum_i \delta N_i = 0$$

$$U = \sum_i E_i N_i \neq \text{const.} \Rightarrow \sum_i E_i \delta N_i \neq 0 \; (= \delta U)$$

$$\delta \ln B = -\sum_i \left(\ln \frac{N_i}{q_i} + 1\right) \delta N_i \overset{(*)}{=} \sum_i \alpha \underbrace{\delta N_i}_{=0} + \beta \sum_i E_i \delta N_i = \beta \cdot \delta U$$

$\delta U = \delta' Q$ za $\delta' A = 0$ $\Rightarrow \delta' Q$ tot. dif. $\Rightarrow$ $\delta \ln B = \beta \delta' Q = \delta \ln B = \delta' \beta Q$ (**)

(**) $\Rightarrow$ II z.t.d. $\Rightarrow dS \geq \frac{\delta' Q}{T}$ IREV. REV.

za REV. $\Rightarrow$ $\delta S = \frac{1}{T} \delta' Q = \frac{1}{TB} \delta \ln B$

$B = \frac{1}{kT}$

$\delta S = k \delta \ln B = \delta(k \ln B)$

$\Rightarrow S = k \cdot \ln B + a^{=0}$

napomena!!!

(**) $\Rightarrow$ toplina $\delta' Q$ pomnožena sa β konstantom

Kanonske raspodjele postaje diferencijalom, štime smo došli do II z.t.d. ~~1. z.t.d.~~ pop. prop.

pop. prop. Supek II 344 $\delta' A = 0$ $\delta U = \sum E_i \delta N_i$ - PSV

Ergodski teorem

→ dosada promatrali sisteme bez interakcije

$G(\mathcal{Q}, p)$ $\quad \mathcal{Q} \equiv \mathcal{Q}_K \quad K = 1, \dots S = 3N$

$p \equiv p_K \quad K = 1, \dots S$

$\langle G \rangle$ - podatak dobiven mjerenjem, tj. mjerimo srednju vrijednost u vremenu opažanja

$$\langle G(\mathcal{Q},p) \rangle = \frac{1}{\tau} \int_{t_0}^{t_0+\tau} G(\mathcal{Q},p)\,dt$$

- za mikroskopske veličine događaji koji se mjer. traju puno manje od trajanja mjerenja - vrijeme jeveliko u usporedbi s događajem (pa možemo uzeti $\tau \to \infty$)

$$\Rightarrow \quad \langle G \rangle = \lim_{\tau \to \infty} \frac{1}{\tau} \int_{t_0}^{t_0+\tau} G(\mathcal{Q},p)\,dt$$

- računski: neodredivo, jer ne možemo znati sve $\mathcal{Q}_k(t)$, $p_k(t)$ $k = 1, \dots S$

- u stat. fizici želimo tu veličinu nadomjestiti statističkom

→ **srednja statist. vrijednost**

- statist. ansambl (≡ hiperravnina u ϕ-prost.) s dosta gustom raspodjelom u faznom Γ prostoru, gdje $\varrho(\mathcal{Q},p,t)$ tj. expl. ovisi o t

općenito $\quad \bar{G}(t) = \int_{\Gamma} G(\mathcal{Q},p)\,\varrho(\mathcal{Q},p,t)\,d\phi$ $\qquad d\phi = d\mathcal{Q}_1 \dots dp_S$

poraste na ∞

- u stanju termodin. ravnoteže ≡ stacion. stanje ni jedna veličina ne ovisi o vremenu

$$\frac{\partial \varrho}{\partial t} = 0 \iff \varrho(\mathcal{Q},p)$$

$$\bar{G} = \int_{\Gamma} G(\mathcal{Q},p)\,\varrho(\mathcal{Q},p)\,d\phi$$

→ veza između $\langle G \rangle$ & $\bar{G}$ ≡ ergodski dm.

dr. Milić

1.3. Fazna gustoća vjerojatnosti:

Γ-prostor $\quad S = s \cdot N$

$$dW = \alpha \cdot dN = \alpha \cdot \varrho(q,p,t)\,d\phi$$

vjerojatnost da odemo pri slučajnom izboru jedne fazne točke iz cijelog faznog ansambla uzeti upravo faznu točku koja se nalazi u elementu faznog volumena $d\phi$ u okolini dane točke $M(q_1 \dots q_s, p_1 \dots p_s)$ faznog prost. Γ

$W = \alpha \cdot \varrho(q,p,t)$ - fazna gustoća vjerojatnosti

$\Rightarrow$ normiranje vjeroj. $\int_\Gamma \alpha \varrho \, d\phi = 1 \Rightarrow \alpha = \left[\int_\Gamma \varrho \, d\phi\right]^{-1}$ Γ - cijeli prostor ili onaj koji stoji na raspolaganju

$\rightarrow$ $\int_\Gamma \varrho \, d\phi$ - ukupan broj faznih točaka u Γ (uvođenjem $\Delta\phi_0 = h^s$ taj broj postaje konačan)

$\rightarrow$ $F(q_1 \dots q_s, p_1 \dots p_s)$ veliče. koja zavisi od dinam. promjenj. mikrostanja npr. Kin. energ. jedne od čestica, impuls, energija interakcije između dvije uočene čestice

$q_i = q_i(q_1^\circ, \dots p_s^\circ, t)$
$p_i = p_i(q_1^\circ, \dots p_s^\circ, t)$
$\Rightarrow F$ je fja. t (za $\forall$ točku) za $\forall$ od sistema uočenog faznog ansambla

bas poput sa plinom u laboratoriju

$$\Rightarrow \bar{F}(t) = \int_\Gamma F(q_1, \dots p_s)\, W(q_1, \dots p_s, t)\, d\phi \qquad (dW)$$

$\rightarrow$ srednja kvadr. fluktuacija

$$\overline{\Delta F^2} = \overline{(F-\bar{F})^2} = \overline{F^2} - \bar{F}^2 = \int_\Gamma (F-\bar{F})^2 W(q_1, \dots p_s, t)\, d\phi$$

$$\delta = 2\sqrt{\overline{(\Delta F)^2}}$$

$$W\{|F-\bar{F}| > a\} \le \frac{\overline{(F-\bar{F})^2}}{a^2} = \frac{\left(\frac{\delta}{2}\right)^2}{a^2}$$

(dokazano Kinčin) - vrpodr. Čebiševa

zakon velikih brojeva - Ljapunov-ljev teorem

$\rightarrow$ kod sistema sa velikim brojem čestica sr. kvadr. fluktuacija je obrnuto proporc. broju čestica tj. ako je ovo mala promatrana fja. $F(t)$ uvijek će se praktično potpuno poklapati sa očekivanom vrijednošću $\bar{F}(t)$

Koliko god puta ponavljali promatr., praktično uvijek ćemo opažati samo $\bar{F}(t)$

Liouville-ov tm. $\Rightarrow \frac{d\varrho(q,p,t)}{dt} = 0$ $\qquad \varrho(q,p,t) = \lim_{\Delta\phi \to 0} \frac{\Delta N}{\Delta\phi}$ (1.3.)

$W = \alpha \cdot \varrho(q,p,t) \quad \Rightarrow \quad \frac{dW}{dt} = 0$

$$\alpha \cdot \frac{\partial W(q,p,t)}{\partial t} + \alpha \cdot \sum_{i=1}^{S} \left[\frac{\partial W}{\partial q_i} \dot{q}_i + \frac{\partial W}{\partial p_i} \cdot \dot{p}_i \right] = 0$$

osnovna jba. evolucije fazne gustoće vjerojatnosti - njenim rješ. uz poč. ograničenje uvjete mogli bismo dobiti najsrpiju moguću statist. distribuciju prom. meh. sistema

2. Ravnotežni ansambli

stat. ansambl - real poč. uvjete od drugih

2.1. Ergodički sistemi

- fizički sistem u termodin. ravnoteži $\Rightarrow \frac{\partial \varrho(q,p,t)}{\partial t} = 0 \Rightarrow \underline{\frac{\partial W}{\partial t} = 0}$

$$\Rightarrow \sum_{i=1}^{S} \left(\frac{\partial W}{\partial q_i} \dot{q}_i + \frac{\partial W}{\partial p_i} \dot{p}_i \right) = 0 \qquad \dot{q}_i = \frac{\partial H}{\partial p_i} \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}$$

$$\sum_{i=1}^{S} \left(\frac{\partial W}{\partial q_i} \cdot \frac{\partial H}{\partial p_i} - \frac{\partial W}{\partial p_i} \cdot \frac{\partial H}{\partial q_i} \right) = [W,H]_{q,p} = 0 \qquad (*)$$

inače: $\frac{dW}{dt} = \frac{\partial W}{\partial t} + [W,H]$ } $\Rightarrow [W,H] = 0$ ili $[W,H] = 0$, $\frac{\partial W}{\partial t} = 0$ } $\Rightarrow \frac{dW}{dt} = 0 \Rightarrow W(q_1 \dots p_S) = C$

Liov. tm. $\frac{dW}{dt} = 0 \wedge \frac{\partial W}{\partial t} = 0$

tj. W je Konst. gibanja sistema

specijalno: H je Konst. gibanja

$\rightarrow$ W je Konst. gibanja sistema

(integral)

$\forall$ repr. Konst. gibanja sistema je neka fja. od sedam osnovnih Konstanti gibanja (integrala)
(integral energije, tri integrala impulsa, tri integrala momenta impulsa)
- sistem ne mora posjedovati svih sedam integrala
- u općem slučaju sistem materijalnih čestica može imati i druge integrale gibanja, ali oni nisu repr. fje. Kanonskih varijabli i za analize nisu od interesa

(*) $\Rightarrow$ Kod sistema u termodin. ravnoteži fazna gustoća vjerojatnosti predstavlja neku fju od sedam osnovnih integrala

ergodički sistemi $\equiv$ W je samo fja. energije

$$\underline{W(q_1 \dots q_S) = \varphi[H(q_1, \dots, p_S)]}$$

Gibbs-ov postulat

(21) b)

$H(q_1, \dots p_s) = E$ **energetska hiperpovršina** (hiperravnina) - igra važnu ulogu u teoriji ergodičkih sistema

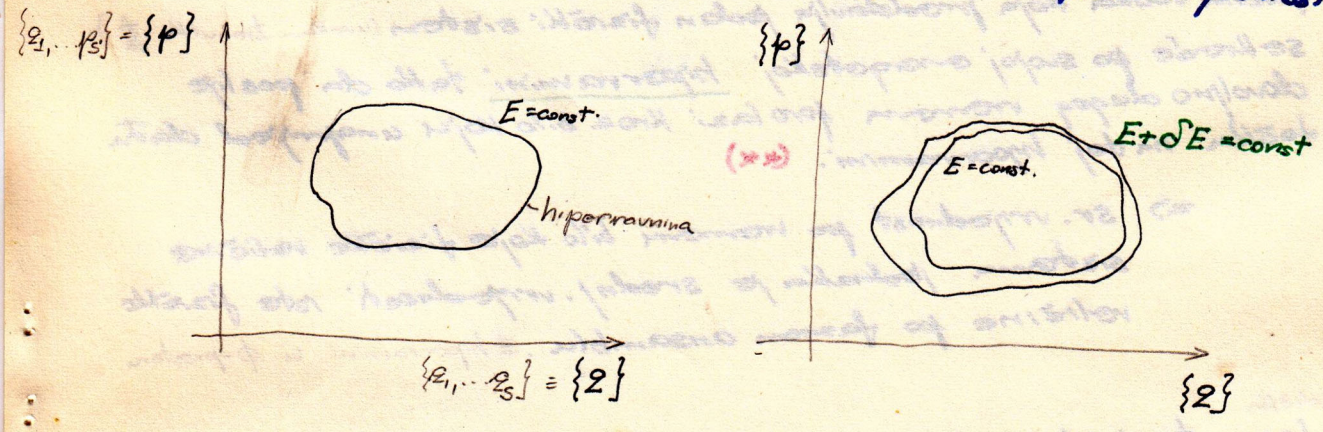
$S = sN$ $\quad H(q_j, p_j, t) = \sum_{j=1}^{S} p_j \dot{q}_j - L(q_j, \dot{q}_j, t)$ $\quad p_j = \frac{\partial L}{\partial \dot{q}_j} \Rightarrow \frac{\partial H}{\partial p_j} = \dot{q}_j - \frac{\partial H}{\partial q_j} = \dot{p}_j$

$\frac{dH}{dt} = \frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t}$

termodin. ravnoteža $\Rightarrow \frac{\partial L}{\partial t} = 0$ $\Rightarrow H(q_j, p_j) = C$ konst. - glasi (vrem. konst.)

ako $L = T - U \Rightarrow H = T + U = E$ za klas. meh. & konz. sile

→ sve fazne tačke koje leže na jednoj ovakvoj hiperravnini odgovaraju fizičkim sredinama čija ukupna energija ima upravo vrijednost E.



$\Gamma(E)$ - volumen Γ prostora ograničen tom hiperravninom

$$\Gamma(E) = \int_{H(q,p) \leq E} d\phi$$

$\frac{\Gamma(E)}{h^S}$ - broj elem. ćelija u $\Gamma(E)$ = razlučivih mikrostanja datog sistema sa energijom ne većom od E

hiperravnine koje odgovaraju energijama E, $E+\delta E$ $\quad (\delta E \ll E)$

$\delta\Gamma(E)$ - volumen tanke hiperljuske

$$\delta\Gamma(E) = \Gamma(E+\delta E) - \Gamma(E) \approx \frac{\partial \Gamma(E)}{\partial E} \cdot \delta E = \Omega(E) \cdot \delta E$$

→ $\Omega(E)$ ima smisao veličine promatrane hiperravnine

→ $\frac{\delta\Gamma(E)}{h^S}$ broj razlučivih mikrostanja fizičkih sistema sa energijama između E & $E+\delta E$

Kao $\frac{dq}{h^s} \leftarrow q_{ri}$

(**) & (*) $\Rightarrow$:

$$\frac{\delta\Gamma(E)}{h^S} = \frac{\Omega(E)}{h^{S'}} \delta E$$

ergodička hipoteza - svi sistemi u termodin. ravnoteži su ergodički,
tj. $W = \alpha S$ je fja. samo energije (*)

- ne može se dokazati
- → vrlo plauzibilna ako se pođe od činjenice da se sistemi u termodin. ravnoteži pokoravaju zakonima termodinamike
- osnovna postavka termodinamike: Makroskopsko stanje sistema, tj: vrijednosti njegovih unutrašnjih parametara u stanju termodin. ravnoteže određeno je vanjskim parametrima i energijom sistema

→ druge formulacije ⇔ navedenoj

- fazna točka koja predstavlja jedan fizički sistem (u nekom trenutku $\bar{t}$) se kreće po svojoj energetskoj hiperravnini tako da poslije dovoljno dugog vremena prolazi kroz bilo koju unaprijed datu točku na toj hiperravnini. (**)

⇒ sr. vrijednost po vremenu bilo koje fizičke veličine sistema jednaka je srednj. vrijednosti iste fizičke veličine po faznom ansamblu. ≡ hiperravnini u ϕ-prostoru

Kvazi ergodička

- fazna trajektorija nekog fizičkog sistema će, poslije dovoljno dugog vremena, proći kroz ma kako malu unaprijed zadanu ε-okolinu bilo koje unaprijed date točke na energetskoj hiperravnini

⇒ svi sistemi u termodin. ravnoteži ergodički ⇒ $W(q_1, \dots p_s) = \varphi[H(q_1, \dots p_s)]$

Gibbs postulat $W = \varphi[H]$ → odrediti oblik fje. φ

odlučenost dijelova sistema:

a) adijabatski sistemi - apsolutno izolirani od vanjskih utjecaja & imaju strogo određ. energiju E

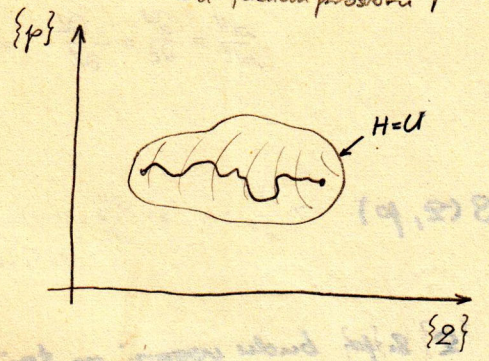
b) izotermni sistemi - nalaze se u kontaktu sa termostatom, tako da imaju fiksiranu T

napomena: ! ⇔ (*) & (**) dokazati

- izolirani sistem energije U

→ niz ekvivalentnih sistema s uvjetom $H = U$

- u faznom prostoru Γ



- krivulja u dvodim. prost. odred. s $H = U$
- općenito hiperploha na kojoj se nalaze sve reprezent. točke stat. ansambla
- → to imamo na hiperplohi niz reprez. stanja → staza na hiperplohi

- pri računanju $\bar{G}^{(t)} = \int_{\Gamma} G(q,p)\,\vartheta(q,p,t)\,dp$

- preko fje. raspodjele uzimamo sve točke s hiperplohe

Ergodska hipoteza Boltzmann 1870.

U toku kretanja reprez. točke (stanja) na vrlo dovoljno dugo vrijeme dolazi u sve točke na promatranoj hiperplohi tj. fazna trajektorija prolaz. kroz sve točke na hiperplohi

⇒ sve točke u vremenu ravnopravne

$$\langle G \rangle = \bar{G}$$

- nije dokazana - čak i netočnost ⇒ ergodski sistem: ne ∃

→ Konstruir. kvazi ergodskih sistema:

Fazna trajektorija dolazi proizvoljno blizu ∀ točki

- uz još neke matem. uvjete kvazi erg. sistem: ∃

⇒ $\langle G \rangle = \bar{G}$ vrijedi

- eksperim. računanje usklađeno sa statist. fizikom i to dalje slaganje

Mikrokanonski i kanonski ansambl

Izgled fje. raspodjele?

$\frac{dH}{dt} = \frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t} = 0$ ako vanjska polja nisu vrem. promjenj.

(i) $\frac{d\varrho}{dt} = 0$ Liouville iz kanonskih jb. $\quad \varrho = \lim_{\Delta\Phi\to 0} \frac{\Delta N}{\Delta\Phi}$

(ii) $\frac{\partial \varrho}{\partial t} = 0$ ravnot. stanja $\Rightarrow \varrho(q,p) \Rightarrow \frac{\partial H}{\partial t} = 0 \Rightarrow \frac{dH}{dt} = 0$ Konst. gib. $\Rightarrow$ Gibbs. postulat

(i) $\Rightarrow \varrho(q,p)$ ograničena uvjetom da $\{q\}$ & $\{p\}$ budu vezani na taj način da trare konstantu gibanja

(*) za izolirane ($U = \text{const}$) sisteme sigurno da je H konst. gibanja

ćim vanjska polja nisu vrem. promjenljiva $\Rightarrow 0 = -\frac{\partial L}{\partial t} = \frac{\partial H}{\partial t} = \frac{dH}{dt} \Rightarrow H(q,p) = U$

$\Rightarrow H = \text{const.} = U$ (*)

postulat Gibbs

$\varrho = \varrho(H)$ tj. $W = \varphi(H)$ gdje $W = \alpha \cdot \varrho$

ergod. hipoteza $\Leftrightarrow$ svi sistemi u termodin. ravnoteži su ergodski tj.

W je fja. samo od energije a ne odvojenih 6-int.

(*) Izolirani i zatvoreni sistemi

(energetski, broja čestica)

$U = H$ $\quad N$ - čestica

predpostavljamo uniformnu raspodjelu na hiperplohi

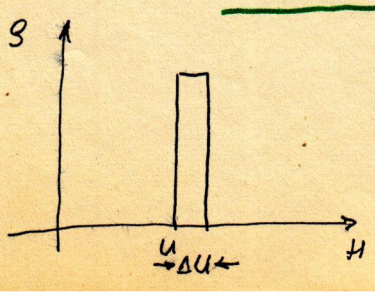
$$\varrho(H) = \begin{cases} \text{const.} & H = U \quad \text{(na hiperplohi)} \\ 0 & H \neq U \end{cases}$$

- time promatramo samo jedan idealan slučaj - nikad nemamo slučaj da je sistem izoliran od okoline, tj. uvijek $\exists$ međudjelovanja $\to$ odvest.

nesigurnost ΔU

$$\varrho(H) = \begin{cases} \text{const.} & U \leq H \leq U + \Delta U \\ 0 & H \neq U \end{cases}$$

mikrokanonska raspodjela



za $\Delta U \to 0 \Rightarrow \varrho(H) = \text{const.}\, \delta(H - U)$

singularna delta fja.

dr. M. Vić

2.2. Mikrokanonski ansambl

po Gibbsu - ansambl fizičkih sistema sa potpuno poznatom energijom E

→ fazne tačke takvih sistema leže najednoj izdvojenoj energetskoj hiperplohi:

$$H = (q_1, \dots p_s, a) = E$$

a - skup vanjskih parametara (volum. sist., vanjsko $\vec{H}$, ...) koji mogu utjecati na oblik i vrijednost H sistema (koji je uvijek fja. od $q_1, \dots p_s$)

sistem u f-dim. ravnot. ergod. hip. → ergod. sistem $\equiv$ $\dot{W} = \varphi(H) = \alpha \cdot \Omega(H) = \alpha\, \delta[E-H]$ (α ali A)

$$\Rightarrow \quad W(q_1, \dots p_s) = A\, \delta[E - H(q_1, \dots p_s, a)]$$

A - faktor normiranja

$dW = w \cdot d\phi$

$$\int_\Gamma dW = 1 \quad \Rightarrow \quad 1 = \int_\Gamma A\, \delta[E - H(q_i, \dots p_s, a)]\, d\phi$$

$$\frac{1}{A} = \int_\Gamma \delta[E - H(q_1, \dots p_s, a)]\, d\phi$$

$u_1 = H(q_1, \dots p_s, a)$ = E hiperploha u Γ' $\qquad u_2, \dots u_{2s}$ proizv. fje. takve da $J \neq 0$

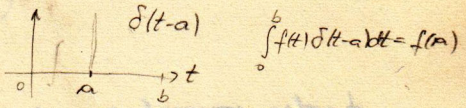
& da zadovoljava uvjete za postojanje inverzne fje.

$\Rightarrow$ $\Gamma_{\text{prostor}} \to \Gamma'$ područje (kin. transformacijama)

energ. hiperploha → koord. površina $u_1 = E = \text{const}$

$$J(u_1, \dots u_{2s}) = J = \frac{\partial(q_1, \dots q_s, p_1, \dots p_s)}{\partial(u_1, \dots u_{2s})} \qquad d\phi = dq_1 \dots dp_s = J\, du_1 \dots du_{2s}$$

$$\Rightarrow \quad \frac{1}{A} = \int_{\Gamma'} \delta[E - u_1] \cdot J\, du_1 du_2 \dots du_{2s}$$



$$\int_0^b f(t)\,\delta(t-a)\,dt = f(a)$$

$\delta(-t) = \delta(t)$ parna fja.

bitno!!! ist. prostor Γ samo druge koordinate

$$= \int_{\Gamma'(u_1)} \cdots \int [J]_{u_1 = E} du_2 \dots du_{2s}$$

($J(E, u_2, \dots u_{2s})$; $2s-1$)

opći volumni element u Γ prostoru, odnosno bilo Γ' prostora (područja)

$$d\phi = du_1 \cdot J\, du_2 \dots du_{2s} = dq_1 \dots dp_s$$

volumni elem. u Γ' područja obzirom na hiperplohu

$$d\phi' = du_1 \cdot \int_{\Gamma'(u_1)} \cdots \int [J]_{u_1 = E = \text{const}} du_2 \dots du_{2s} = du_1 \cdot \Omega(E, a)$$

($2s-1$; neodvojeno Γ')

zbog različ. a različ. je fja $H = u_1$ pa dakle $J(u_1, \dots u_{2s})$

→ različ. energ. hiperploha $u_1 = E = \text{const}$.

$\Omega(E, a)$ ... razlika Γ i Γ'

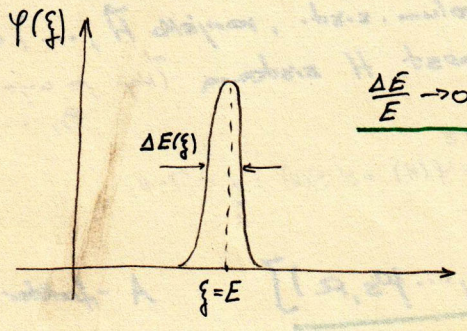
$$\delta\Gamma(E) = \Gamma(E + \delta E) - \Gamma(E) \approx \frac{\partial \Gamma}{\partial E} \cdot \delta E = \Omega(E)\, \delta E$$

$$\Gamma(E) = \int_{H(q,p) \le E} d\phi$$

$$\Rightarrow \quad \frac{1}{A} = \Omega(E,a)$$

$$W(\mathcal{Q}_1, \dots p_3) = \frac{1}{\Omega(E,a)} \cdot \delta[E - H(\mathcal{Q}_1, \dots p_3, a)]$$

$W = \varphi(H) \quad \Rightarrow \varphi(H) = \frac{1}{\Omega(E,a)} \delta[E - H(\mathcal{Q}_1, \dots p_3, a)] \qquad H \leftrightarrow \xi$



$\frac{\Delta E}{E} \to 0$

$$\int_{-a}^{+a} \varphi(\xi) d\xi = \frac{1}{\Omega(E,a)} \cdot 1 = \text{const.}$$

2.3. Kanonski ansambl

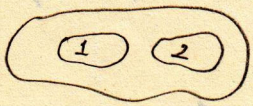
→ ansambl faznih točaka koje reprezentiraju, u faznom prostoru Γ, identične fizičke sisteme konst. temp. T

→ spremnik ima mnogo više čestica nego sistem ⇒ fluktuacije energije sistema neutječe na T spremnika

→ slaba interakcija između sistema & spremnika

tj. energ. interakcije $\ll \Sigma$ energ. sistema & spremnika

2 sist. u kontaktu sa spremnikom, ali međ. izolirana



- čak i u energ. smislu, jer spremnik je ogroman sprem njih, pa promjene E jednog neutječu na drugi.

$+$-din. ravnoteža ⇒

$$W_1[\mathcal{Q}_1^{(1)} \dots p_{s_1}^{(1)}] = \varphi_1[H_1(\mathcal{Q}_1^{(1)} \dots p_{s_1}^{(1)})] \qquad S_1 = s_1 \cdot N_1$$

$$W_2[\mathcal{Q}_1^{(2)} \dots p_{s_2}^{(2)}] = \varphi_2[H_2(\mathcal{Q}_1^{(2)} \dots p_{s_2}^{(2)})] \qquad S_2 = s_2 \cdot N_2$$

izolirani sustavi međ. ⇒

$$W_{12}[\mathcal{Q}_1^{(1)} \dots p_{s_1}^{(1)} \mathcal{Q}_1^{(2)} \dots p_{s_2}^{(2)}] = W_1[\mathcal{Q}_1^{(1)} \dots p_{s_1}^{(1)}] \cdot W_2[\mathcal{Q}_1^{(2)} \dots p_{s_2}^{(2)}] \qquad d\phi_1 \cdot d\phi_2 \quad d\phi_1 \quad d\phi_2$$

vjerojatnost da istovremeno sistemi imaju $H_1 = E_1 \quad H_2 = E_2$

→ naime W_1 je vjerojatnost da sustav (1) ima $E_1 = H_1$ & da je baš taj H_1 određen sa jednim određenim slogom $(\mathcal{Q}_1^{(1)} \dots p_{s_1}^{(1)})$

(22) b)

$H_{uk} = H_1 + H_2 + H_{12} \approx 0$

$W_{12} = F(H_1 + H_2)$

(1) & (2) čine nov sistem u t-din. ravnotež. ukupne energije $H_1 + H_2$

$\Rightarrow$ ergodski sistem $W = F(H_{uk.})$

$\Gamma^{(1)}$ & $\Gamma^{(2)} \Rightarrow \Gamma^{(1,2)}$ dimenzije $2S_2 + 2S_1 = 2s_1N_1 + 2s_2N_2$

$\rightarrow$ ali ukojem se hiperplohe iz pojedinačnih faznih prostora nedovezuju, a live sijeku

$$\Rightarrow \quad F(H_1+H_2) = \varphi_1(H_1) \cdot \varphi_2(H_2) \quad / \ln, d$$

(derivacija po ogrlom argumentu $H_1 + H_2$)

$$\frac{F'(H_1+H_2)}{F(H_1+H_2)} d(H_1+H_2) = \frac{\varphi_1'(H_1)}{\varphi_1(H_1)} dH_1 + \frac{\varphi_2'(H_2)}{\varphi_2(H_2)} dH_2$$

$(dH_1 + dH_2)$

H_1 & H_2 proizvoljni $\Rightarrow$ nezav. varijable (*) $\Rightarrow$

$$\frac{F'(H_1+H_2)}{F(H_1+H_2)} = \frac{\varphi_1'(H_1)}{\varphi_1(H_1)} = \frac{\varphi_2'(H_2)}{\varphi_2(H_2)} \overset{(*)}{=} \beta$$

$\swarrow$ tj. sistemi (1) & (2) statistički nezavisni

$\rightarrow$ ovisi od karakteristika spremnika

$\frac{d\varphi(H)}{dH} = \beta\varphi(H) \quad \frac{d\varphi(H)}{\varphi(H)} = \beta dH \quad \ln\varphi(H) = \beta H + \ln A \quad \Rightarrow \varphi(H) = Ae^{\beta H}$

$\Rightarrow \varphi(H) = Ae^{\beta H}$

$W = d\Sigma(H)$

$$W(q_1 \dots p_s, a) = A e^{\beta H(q_1 \dots p_s, a)}$$

označava skup svih parametara koji utječu na H

vjerojatno se ne popunjuje radom ? normiranja ipak se popunjuje

$\rightarrow$ mikrostanja unutar fazne ćelije $\Delta\phi_0 = h^s$ ne mogu se razlikovati

stavljamo $A = A' \cdot h^{-s}$

jer $dW = W\, d\phi = Ae^{\beta H} d\phi = A' e^{\beta H} \left(\frac{d\phi}{h^s}\right)$ broj ćelija volumena $d\phi$

$\rightarrow$ fazna gustoća vjerojatnosti mora opadati s energijom $\Rightarrow \beta < 0$

$$\beta = -\frac{1}{\theta}$$

θ - modul Kanonske raspodjele

$$\Rightarrow dW = \frac{A'}{h^s} e^{-\frac{1}{\theta}H(q_1 \dots p_s, a)} d\phi \qquad (*)$$

$\rightarrow$ fizički sistemi sa N identičnih čestica $\Rightarrow$ razmjena mjesta dviju čestica suštinski ne mijenja probitno mikrostanje $\Rightarrow A' = \frac{1}{N!} \cdot \frac{1}{Z}$ $\Rightarrow dW = \frac{1}{N!}\frac{1}{Z} e^{\beta H} \frac{d\phi}{h^s}$

$$dW = \frac{1}{N!\,h^s} \cdot \frac{1}{Z} e^{-\frac{1}{\theta}H(q_1 \dots p_s, a)} d\phi \qquad (**)$$

(*)

$\rightarrow$ sa formalnog stanovišta (*) & (**) ekvivalentni jer se A' & Z odreduju iz uvjeta normiranja tako da uvijek dobijamo isti izraz za dW normiranu

⇒ normirana vjerojatnost

$$dW = \frac{e^{-\frac{1}{\theta}H(q_1,\dots p_3,a)}\,d\phi}{\int_\Gamma e^{-\frac{1}{\theta}H(q_1,\dots p_3,a)}\,d\phi}$$

→ sa fizičkog stanovišta prioritet ima (**) pred (*) $\quad 1 = \int_\Gamma dW = \int_\Gamma \frac{1}{N!\,h^{3s}}\,\frac{1}{Z}\,e^{-\beta H}\,d\phi$

$$\Rightarrow \quad Z = \frac{1}{N!\,h^{3s}} \int_\Gamma e^{-\frac{1}{\theta}H(q_1,\dots p_3,a)}\,d\phi$$

statistička suma sistema (integral stanja) **u kontaktu sa spremnikom** igra prim. ulogu u odn. termodin.

Uvedimo:

$$Z = e^{-\frac{\psi}{\theta}} \qquad \psi = -\theta \ln Z$$

(**) ⇒

$$dW = \frac{1}{N!\,h^{3s}}\, e^{\frac{1}{\theta}[\psi - H(q_1,\dots p_3,a)]}\,d\phi \qquad (***)$$

→ često umjesto $w = \frac{dW}{d\phi}$ primjenjuje izraz za gustoću vjerojatnosti energije $W(E)$

$F(x_1,\dots x_n)$ poznata fja. & $W(x_1,\dots x_n)$ fja. raspodjele (gustoća) vjerojatnosti tih slučajnih varijabli $x_1 \dots x_n$

⇒ srednja (očekivana) vrijednost veličine F

(ispravno za sebe) → $\bar{F} = \int_{(x)} F(x_1,\dots x_n)\,W(x_1,\dots x_n)\,dx_1 \dots dx_n \qquad (*)$ — gdje se integrira po čitavom području (x) varijabli $x_1 \dots x_n$

formalno (ispravno za sebe) → $\bar{F} = \int_{(F)} F\,W(F)\,dF \qquad (**)$ $W(F)$ gustoća vjerojatnosti veličine F, a integrira se po svim vrijednostima koje F poprima, tj. području (F)

gdje $(***)$ $W(F) = \int_{(x)} \delta[F - F(x_1,\dots x_n)]\,W(x_1,\dots x_n)\,dx_1 \dots dx_n \overset{!}{=} \int_{(x)} [W(x_1,\dots x_n)]_{F(x_1,\dots x_n)=F}\,dx_1 \dots$ zbog višestrukog integrala

tj. takve vrijednosti $(x_1,\dots x_n)$ da je ispunjeno $F = F(x_1,\dots x_n)$

dokaz:

$$\bar{F} = \int_{(F)} F \left\{ \int_{(x)} \delta[F - F(x_1,\dots x_n)]\,W(x_1,\dots x_n)\,dx_1 \dots dx_n \right\} dF =$$

$$\overset{(*1)}{=} \int_{(x)} W(x_1,\dots x_n) \left\{ \int_{(F)} F\,\delta[F - F(x_1,\dots x_n)]\,dF \right\} dx_1 \dots dx_n = \int_{(x)} W(x_1,\dots x_n)\,F(x_1,\dots x_n)\,dx_1 \dots dx_n$$

$[F]_{F=F(x_1,\dots x_n)}$

Vrijedi $\int_{-a}^{a} x\,\delta(x - x_1)\,dx = [x]_{x=x_1} = x_1$

(*1) zamjena redoslijeda integracija dozvoljena za konvarg. integrale

Dokaz: (*) ⇔ (**) & (***)

(22) c)

$W = \varphi(H)$

$H = H(q_1, \dots p_s, a) = E$ $\qquad \frac{dW}{d\phi} = W(q_1, \dots p_s, a) = \frac{1}{N!\,h^s}\, e^{\frac{1}{\theta}[\psi - H(q_1, \dots p_s, a)]}$

to je gustoća vjerojatnosti da sustav ima H baš od sloga $(q_1, \dots p_s)$ i jasno da je još $H = E$, jer zaista E mogu biti realizirani slučajni dok je vjerojatnost $W \cdot d\phi$

$\bar{E} = \bar{H} = \int_\Gamma H(q_1, \dots p_s, a)\, W(q_1, \dots p_s, a)\, d\phi$

$\bar{E} = \int_{(E)} E\, W(E)\, dE$

$W(E)$ - gustoća vjerojatnosti E, tj. da sustav ima $H = E$ s tim da je svejedno od kojeg sloga je $H(q_1, \dots p_s)$

vjerojatnost $W(E)\,dE$

$W(q_1, \dots p_s, a)\, d\phi$

$$\Rightarrow W(E) = \int_\Gamma \delta[E - H(q_1, \dots p_s, a)] \cdot \frac{1}{N!\,h^s}\, e^{\frac{1}{\theta}[\psi - H(q_1, \dots p_s, a)]}\, d\phi$$

uvedimo $u_1 = H(q_1, \dots p_s, a)$ $\quad u_2, \dots u_{2s}$ tako da $J = \frac{\partial(q_1, \dots p_s)}{\partial(u_1, \dots u_{2s})} \neq 0$

$\Rightarrow$ Γ prostor $\to$ Γ' područje $\qquad d\phi = dq_1 \cdots dp_s = J\, du_1 \cdots du_{2s}$

$$W(E) = \frac{1}{N!\,h^s} \int_{\Gamma'} \delta[E - u_1] \cdot e^{\frac{1}{\theta}[\psi - u_1]} \cdot J\, du_1\, du_2 \dots du_{2s} =$$

$$= \frac{1}{N!\,h^s} \int_{\Gamma'^{2s-1}} \cdots \int e^{\frac{1}{\theta}(\psi - E)} \cdot [J]_{u_1 = E}\, du_2 \cdots du_{2s}$$

$$= \frac{1}{N!\,h^s} \cdot e^{\frac{\psi - E}{\theta}} \cdot \underbrace{\int_{\Gamma'^{2s-1}} \cdots \int [J]_{u_1 = E}\, du_2 \cdots du_{2s}}_{= \Omega(E, a)} \quad \text{veličina energ. hiperplohe } u_1 = E = \text{konst}$$

$$\boxed{W(E) = \frac{1}{N!\,h^s} \cdot e^{\frac{\psi - E}{\theta}}\, \Omega(E, a) = \frac{1}{N!\,h^s} \cdot \frac{1}{Z}\, e^{-\frac{E}{\theta}}\, \Omega(E, a)}$$

gustoća vjerojatnosti kanonskog ansambla

$$1 = \int_{(E)} W(E)\, dE \quad \Rightarrow$$

$$Z = \int_{(E)} \frac{1}{N!\,h^s}\, e^{-\frac{E}{\theta}}\, \Omega(E, a)\, dE$$

$$\boxed{Z = \frac{1}{N!\,h^s} \int_{(E)} e^{-\frac{E}{\theta}}\, \Omega(E, a)\, dE}$$

statistička suma sustava

dana preko integracije po svim E

$\Omega(E, a)$ veličina energ. hiperplohe koja odgovara energiji E

$\to$ $W(E)$ ima dva faktora zavisna od E

prvi naglo pada, a drugi raste brzo sa E $\Rightarrow$ ima oštar maximum za neki E_0

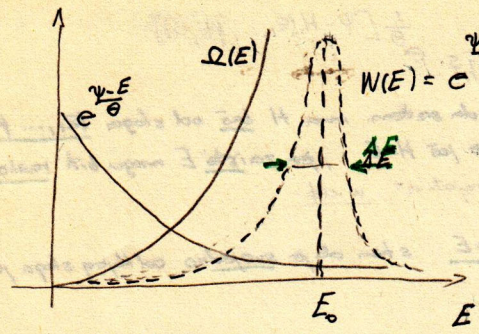
- max. to oštriji što je broj čestica N veći:

$$\boxed{W(E) \to \delta(E - E_0) \quad \text{kad } N \to \infty}$$

tj. kanonski ansambl za velik broj čestica prelazi u mikrokanonski

$E = U$

$d\Phi = dU - \Omega(E)$



bitno !!!

1° $\lim_{N\to\infty} \frac{\Delta E}{E} \to 0$

2° $\int_{(E)} \frac{1}{N!h^{3N}} \cdot e^{\frac{\psi-E}{\theta}} \Omega(E)\, dE = \int_{(E)} W(E)\, dE = 1$ $\Rightarrow$

kanon. ans. mikrokan. ans.

$\Rightarrow \lim_{N\to\infty} W(E) = \delta(E - E_0)$ za makroskopske tijela $N \gg 1$

relativna fluktuacija - oštrina maksimuma kod $W(E)$

$\frac{\Delta E}{\bar{E}} \approx \sqrt{\frac{\overline{\Delta E^2}}{\bar{E}^2}} \overset{*)}{=} \sqrt{\frac{\partial(\frac{1}{\theta})}{\partial(\frac{1}{\theta})}} \sim \frac{1}{\sqrt{N}} \Rightarrow \frac{\Delta E}{\bar{E}} \to 0$

tj. fizički sistem predstavljen kanonskim ansamblom praktično se uvijek nalazi u stanju sa $E_0 = \bar{E}$

Ljapunov-teorem zakon velikih brojeva → sr. kvadr. fluktuacija obrnuto prop. broju čestica

iz $W(E)$ $\int_{(E)} W(E)\, dE = 1$ dobili smo Z

Dokaz: počinjemo od Z

$$Z = \frac{1}{N!h^s} \int_{(E)} e^{-\frac{E}{\theta}} \Omega(E,a)\, dE \quad / \frac{\partial}{\partial(\frac{1}{\theta})}$$

$$\frac{\partial Z}{\partial(\frac{1}{\theta})} = -\frac{1}{N!h^s} \int_{(E)} E e^{-\frac{E}{\theta}} \Omega(E,a)\, dE$$

$$\frac{\partial Z}{\partial(\frac{1}{\theta})} = -Z \frac{\int_{(E)} E e^{-\frac{E}{\theta}} \Omega(E)\, dE}{\int_{(E)} e^{-\frac{E}{\theta}} \Omega(E)\, dE} = -\bar{E}$$

$\bar{E} = \int_{(E)} E\, W(E)\, dE$

$\bar{E} = \frac{1}{N!h^s} \cdot \frac{1}{Z} \int_{(E)} E e^{-\frac{E}{\theta}} \Omega(E)\, dE$

$\bar{E} = \frac{\int_{(E)} E e^{-\frac{E}{\theta}} \Omega(E)\, dE}{\int_{(E)} e^{-\frac{E}{\theta}} \Omega(E)\, dE}$

$$\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial(\frac{1}{\theta})} = -\left(\frac{\partial}{\partial\beta} \ln Z\right)_V \qquad \beta = \frac{1}{\theta}$$

$$\frac{\partial^2 Z}{\partial(\frac{1}{\theta})^2} = \frac{1}{N!h^s} \int_{(E)} E^2 e^{-\frac{E}{\theta}} \Omega(E)\, dE = Z \cdot \frac{\int_{(E)} E^2 e^{-\frac{E}{\theta}} \Omega(E)\, dE}{\int_{(E)} e^{-\frac{E}{\theta}} \Omega(E)\, dE}$$

$\overline{E^2}$

$$\overline{E^2} = \frac{1}{Z} \cdot \frac{\partial^2 Z}{\partial(\frac{1}{\theta})^2}$$

$\overline{E^2} - 2\bar{E}\,\overline{(E)} + \bar{E}^2 = \overline{E^2} - \bar{E}^2$

$$\frac{\partial \bar{E}}{\partial(\frac{1}{\theta})} = \frac{1}{Z^2} \cdot \left(\frac{\partial Z}{\partial(\frac{1}{\theta})}\right)^2 - \frac{1}{Z} \frac{\partial^2 Z}{\partial(\frac{1}{\theta})^2} = \bar{E}^2 - \overline{E^2}$$

$\overline{(\Delta E)^2} = \overline{(E - \bar{E})^2} = \overline{E^2} - \bar{E}^2$

$$\Rightarrow \frac{\overline{(\Delta E)^2}}{\bar{E}^2} = \frac{\overline{E^2} - \bar{E}^2}{\bar{E}^2} = \frac{-\frac{\partial \bar{E}}{\partial(\frac{1}{\theta})}}{\bar{E}^2} = \frac{\partial(\frac{1}{\bar{E}})}{\partial(\frac{1}{\theta})}$$

originalno !!!

$*)$ $W\{|E - \bar{E}| > \bar{E}\} \leq \frac{\overline{\Delta E^2}}{\bar{E}^2}$ $\xrightarrow{N\to\infty}$ 0

čestica razmišlja → Ljapunov teorem

papir pokaži iz izračunatog $\Omega(E,A)$

*) je obrnuto proporcionalan broju čestica N sistema, jer $\bar{E} \sim N$ u tom sistemu gdje čestice slabo interagiraju (međutim to nije u vezi sa činjenicom da se radi o kanonskom ansamblu: da bi fizički sistem bio prikazan u faznom prostoru točkom koja pripada kanonskom ansamblu potrebno je da je taj sistem u slaboj interakciji sa spremnikom, pa pretpostavka o slaboj interakciji među česticama fizič. sistema predstavlja dopunsku hipotezu koja je u velikom broju slučajeva zadovoljena ali kod plazme nije uvijek.)

vjerojatno da čestica ima svoju energiju

*) ako je potenc. energija kvadratična fja. koordinata $\Rightarrow \bar{E}_{pot} \sim N \cdot \frac{\theta}{2}$

$$W(E) = \frac{1}{N!h^s} \cdot \frac{1}{Z} e^{-\frac{E}{\Theta}} \Omega(E,a) \qquad Z = \frac{1}{N!h^s} \int_{(E)} e^{-\frac{E}{\Theta}} \Omega(E,a)\, dE$$

$$\bar{E} = \frac{\int_0^\infty E\, \Omega(E,a) e^{-\frac{E}{\Theta}} dE}{\int_0^\infty \Omega(E,a) e^{-\frac{E}{\Theta}} dE} = \frac{\int_0^\infty E e^{-\beta E} \Omega(E,a) dE}{\int_0^\infty e^{-\beta E} \Omega(E,a) dE}$$

$$\bar{E} = -\frac{\partial}{\partial \beta} \ln \left(A \int_0^\infty e^{-\beta E} \Omega(E,a)\, dE \right) = -\left(\frac{\partial}{\partial \beta} \ln Z \right)_V$$

$$\Omega(E) = \frac{d\phi(E)}{dE} =$$

idealni plin $\quad \phi(H) = V^N \cdot C \cdot (2mH)^{\frac{3N}{2}}$

$$\frac{d\phi(H)}{dH} = 3Nm\, C V^N (2mH)^{\frac{3N}{2}-1}$$

protp. N-paran $\Rightarrow Z = ACV^N (2mKT)^{\frac{3N}{2}} \left(\frac{3N}{2}\right)!$ str. 89

$$Z = \text{const.} \cdot \beta^{-\frac{3N}{2}}$$

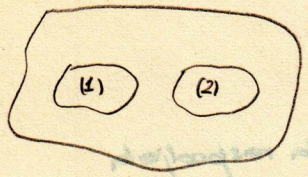
$$\Rightarrow \bar{E} = -\frac{\partial}{\partial \beta} \left[-\frac{3N}{2} \ln \beta \right] = \frac{3N}{2} \cdot \frac{1}{\beta} = \frac{3N}{2} KT$$

$$\bar{E} = \frac{3}{2} KT \cdot N \qquad \Rightarrow \bar{E} \sim N$$

→ pokaži da to vrijedi i za realni plin, ako je potencijalna energija oblika αr^2

⇒ očito dala iz ekvipartičionog tm. (budući se radi o harmoničkim sitama-oscilacijama) još za svaki stupanj slobode dolazi KT

Zatvoreni Sistemi u termičkoj ravnoteži s okolinom



- izmjenjuju energiju ali termostat se brine da temp. ostaje konstantna

T, N - broj čestica

uzimamo niz takvih podsistema → kakva je dja. raspodjele za te podsistema

* **podsistemi:** - Distribuciona dja. u stat. ansamblu za podsistema (1) & (2)

(1) H_1, S_1, ϕ_1

(2) H_2, S_2, ϕ_2

→ **shvatimo (1) & (2) kao cjelinu**

$$H = H_1 + H_2 + H_{12}$$ - interakcije međusobne

podsistema zanimljivo još uvijek makroskopskim → velik broj čestica

H_1 - zbroj podsistema prop. broju čestica dj. opisuje ukupni volumen

H_{12} = interakcije opisuje čestice na površini koje su u interakciji sa okolinom

$$\rightarrow \frac{H_{12}}{H_1} \approx \frac{N^{2/3}}{N} = \frac{1}{\sqrt[3]{N}} \Rightarrow H_{12} \ll H_1 \text{ za } N \gg$$

naime: $V \sim N$

$P \sim (\sqrt[3]{V})^2 \sim N^{2/3}$

$$\Rightarrow H = H_1 + H_2$$

→ **zanemarivanjem interakcije → dogovorili: u (1) odvijanje se neovisno** *) **od (2)**

Kao kod idealnog plina - ukupna energija dvaju molekula je jednaka zbroju

- iz aditivnosti energije → exp. zakon koji karakt. tu raspodjelu

$$\Rightarrow d\Gamma \overset{*)}{=} d\Gamma_1 \cdot d\Gamma_2 \qquad d\phi = d\phi_1 \cdot d\phi_2$$

ukupna vjerojatnost, zapravo

opć. $d\Gamma = \alpha S d\phi$

ukupni fazni prostor shvaćen kao zbroj faznih prostora podsistema

$$\Rightarrow S d\phi = S_1 d\phi_1 S_2 d\phi_2$$

$$S(\underbrace{H_1 + H_2}_{H}) = S_1(H_1) \cdot S_2(H_2)$$

$$\ln S = \ln S_1 + \ln S_2 \quad / : \frac{\partial}{\partial H_1}$$

$$\Rightarrow \frac{\frac{\partial S}{\partial H_1}}{S} = \frac{\frac{dS_1}{dH_1}}{S_1}$$

$$H = H_1 + H_2 \Rightarrow \frac{\partial S}{\partial H_1} = \frac{\partial S^{(H)}}{\partial H} = \frac{dS^{(H)}}{dH}$$

$$\Rightarrow \frac{1}{S}\frac{dS^{(H)}}{dH} = \frac{1}{S_1} \cdot \frac{dS_1^{(H_1)}}{dH_1}$$

analogno i za $\frac{\partial}{\partial H_2}$

H_1 & H_2 nezav. varijable

invarijantna veličina $\frac{1}{\varrho}\frac{d\varrho}{dH} = \frac{1}{\varrho_1}\frac{d\varrho_1}{dH_1} = \frac{1}{\varrho_2}\frac{d\varrho_2}{dH_2} = -\frac{1}{\vartheta}$

za sistem koji se nalazi u t-din. ravnoteži: $\frac{d\varrho}{\varrho} = -\frac{dH}{\vartheta} \Rightarrow \ln\varrho = \ln C + \frac{H}{\vartheta}$

$$\Rightarrow \varrho(H) = C e^{-\frac{H}{\vartheta}}$$ Kanonska raspodjela

$$\int_\Gamma d\mathcal{W} = 1 \Rightarrow C\int_\Gamma e^{-\frac{H}{\vartheta}} d\phi = 1$$

$-\frac{1}{\vartheta}$ → negativan izbor da bi integral konvergirao ili Σ prostor energija

$\vartheta > 0$

$$\varrho(H) = A e^{\frac{\psi - H}{\theta}}$$

ψ - odgovara slob. energiji

θ - odgovara temperaturi

→ modul Kanonske raspodjele ili: statist. temperatura

Def: Neki sistem ima statističku temperaturu θ, ako je vjerojatnost da sistem nađemo u vol. elementu $d\phi$ dana sa

$$d\mathcal{W} = A e^{\frac{\psi - H}{\theta}} d\phi \qquad A = \frac{1}{N!\,h^s}$$

→ ne možemo govoriti o statističkoj temperaturi malog broja čestica

→ vjerojatnost zbivanja u sistemu kojeg čine (1) & (2)

$d\mathcal{W} = d\mathcal{W}_1 \cdot d\mathcal{W}_2 \quad d\phi = d\phi_1 \cdot d\phi_2$

$$\varrho = \varrho_1 \cdot \varrho_2 \sim e^{\frac{\psi_1 - H_1}{\theta_1} + \frac{\psi_2 - H_2}{\theta_2}}$$

1) $\theta_1 = \theta_2 = \theta$ tj. (1) & (2) na istoj statističkoj temperaturi

$$\Rightarrow \varrho(H) \sim e^{\frac{\psi_1 + \psi_2}{\theta} - \left(\frac{H_1 + H_2}{\theta}\right)}$$

velik broj čestica u (1) & (2) $\Rightarrow H_2 \ll H_1$

$\Rightarrow H = H_1 + H_2$ Konstanta gibanja jer su H_1 & H_2 konst. gibanja

$\Rightarrow$ raspodjela ϱ se ne mijenja s vremenom, tj. konst. je gibanja

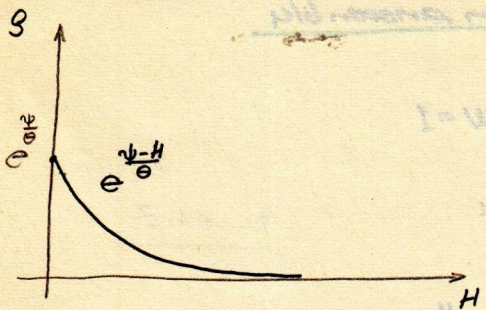
2) $\theta_1 \neq \theta_2$

$$\varrho(H) \sim e^{\frac{\psi_1}{\theta_1} + \frac{\psi_2}{\theta_2} - \left(\frac{H_1}{\theta_1} + \frac{H_2}{\theta_2}\right)}$$

$\left(\frac{H_1}{\theta_1} + \frac{H_2}{\theta_2}\right)$ nije konstanta gibanja jer se θ_1 & θ_2 mijenjaju zbog (*)

(*) ne daje Kanonsku raspodjelu za $H = H_1 + H_2$ ni pod kojim uvjetima

- za vrijeme izjednačavanja temp. mijenja se i fja. raspodjele



$$\varrho = A e^{\frac{\Psi - H}{\Theta}}$$

- pobuđenje exp. opada s rastom energije H
- u Kanonskim Koord. sistemima najviša pobuđena stanja su za $H=0$

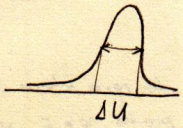
- elementi kan. ansambla imaju različite energije ($\forall$ točka Γ prostora ima $\neq$ koordinate $\Rightarrow \neq H$ osim za hiperplohu

→ kod mikrokan. ansambla svi elementi unutar $U, U+\Delta U$ imaju sve egzaktnu energiju

→ srednja vrijednost:

fja. raspodjele kanonskog se srednja vrijednost energije kanonskog ansambla gomila oko one računate pozadinsko-fizikalne, gdje je disperzija najmanja (srednje energije)

- za sistem od N čestica



$$\frac{\Delta U}{\bar{U}} \propto \frac{1}{\sqrt{N}}$$ (mjera disperzije) — dokazano u 22 c) *)

→ $\bar{U}$ reprezentira vrij. energije u Kanonskom ansamblu jer je disperzija oko nje toliko mala

→ termodin. veliš. možemo izraziti preko Kanonskog i mikrokan. ansambla

Matematički je jednostavnije računanje preko Kanonskog ansambla

→ odredit. T kod Kanonskog ansambla dovodimo na sr. vrij. energije
→ egzaktu vrijednost T za mikrokanonski ansambl

Rezime: - u zanemarivanju interakcije nesmijemo je potpuno zanemariti tako da čitavo razmatranje svedemo na idealni plin, već samo interakciju između dva podsistema u kontaktu za termodinamiku

Kanonska raspodj.: $\varrho \sim e^{-\frac{H}{\Theta}}$ — $\dim$ energije ista T

Boltzmanova raspodj.: $\varrho \sim e^{-\frac{E}{kT}}$ — E - ukupna energija sistema ali koja nikada ne može poprimiti od interakcije među čestica; T - t-dim. temperatura

Kanonska za $\Theta = kT$: $\varrho \sim e^{-\frac{H}{kT}}$ — H - zbroj energija pojedinih sistema, ali koja može ali ne mora poprimiti od međusobne interakcije čestica

spec. slučaj Kanonske!

jer pretpostavke za uvođenje Kanonske raspodjele zadovoljene su idealnim plinom

$\forall$ čestica idealnog plina neovisna o drugima pa čini jedan podsistem, i ravnamo potrebe kazati o zavoru interakcije jer ta proizlazi iz idealnog plina

Velikokanonski ansambl

- niz sistema kod kojih broj čestica nije konstantan - izmjenjivanje čestica (kao u Kanonskom mogućnost izmjene energije)
- za analizu t-dim. procesa sistema koji su otvoreni - kemijski proces.!

Gibbs uveo { m.k. K v.k.

Srednje vrijednosti fiz. veličina u kanonskom ansamblu

$$\varrho = A e^{\frac{\Psi - H}{\Theta}} \qquad dW = \varrho \, d\phi \qquad \int_\Gamma dW = 1$$

$$A e^{\frac{\Psi}{\Theta}} \int_\Gamma e^{-\frac{H}{\Theta}} d\phi = 1 \quad \Rightarrow \quad A e^{\frac{\Psi}{\Theta}} = \left(\int_\Gamma e^{-\frac{H}{\Theta}} d\phi \right)^{-1} \qquad \Psi = -\Theta \ln Z$$

$$\Rightarrow \varrho = \frac{e^{-\frac{H}{\Theta}}}{\int_\Gamma e^{-\frac{H}{\Theta}} d\phi} \qquad dW = \frac{e^{-\frac{H}{\Theta}} d\phi}{\int_\Gamma e^{-\frac{H}{\Theta}} d\phi}$$

formalno sasvim isto kao i Boltzmannova raspodjela

$$\Rightarrow \bar{G}(z,p) = \int_\Gamma G(z,p) \, dW = \frac{\int_\Gamma G(z,p) e^{-\frac{H(z,p)}{\Theta}} d\phi}{\int_\Gamma e^{-\frac{H(z,p)}{\Theta}} d\phi}$$

Fja. particije

$$Z = A \int_\Gamma e^{-\frac{H}{\Theta}} d\phi \qquad A = \frac{1}{N! h^s}$$

da igra ulogu fje particije dobivamo preko $\Psi \equiv F$ na (24) c)

→ na sistem djeluju opće sile s općim koordinatama

Koord.	$r_1, r_2, r_3, \ldots$	V
Opće sile.	$R_1, R_2, R_3, \ldots$	P

$$R_i = -\frac{\partial H}{\partial r_i}$$

na (24) a) relacije i)

Srednja vrijednost opće sile:

$$\bar{R}_i = \int_\Gamma R_i \, dW = -A \int_\Gamma \frac{\partial H}{\partial r_i} \cdot e^{\frac{\Psi - H}{\Theta}} d\phi = -\left(\frac{\partial \Psi}{\partial r_i} \right)_{\Theta, r_1, \ldots r_{i-1}, r_{i+1}, \ldots}$$

$$\int_\Gamma dW = 1 \Rightarrow A \int_\Gamma e^{\frac{\Psi - H}{\Theta}} d\phi = 1 \quad / \frac{\partial}{\partial r_i}$$

$$A \frac{\partial \Psi}{\partial r_i} \int_\Gamma e^{\frac{\Psi - H}{\Theta}} d\phi - \underbrace{A \int_\Gamma \frac{\partial H}{\partial r_i} e^{\frac{\Psi - H}{\Theta}} d\phi}_{\bar{R}_i} = 0$$

→ sličnost s Maxw. relacijama (npr. $P = -\left(\frac{\partial F}{\partial T}\right)_V$) → veza Ψ sa slob. energijom F

Ar. Milić

3. Statistička termodinamika

termodinamika - makroskop. osobine fizičkih sistema u stanju ravnoteže

- ako se makroskop. stanje mijenja s vremenom → mučno promjene dolikuje spore da u t i t+Δt sistem ima mogućnost da dođe u ravnotežno stanje (koje odgovara trenutnim vrijednostima vanjskih parametara)

→ „kvazistacionarni" ili „reverz. procesi"

→ - primjer: idealan plin:

- t-din. ravnot. kad se uspostavi $\vec{v}$ & T & Maxw. raspodj. po $\vec{v}$ const. u cijeloj masi plina
- vrijeme uspostavljanja ovakvog stanja $\approx \Delta t$ između dva sudara (kolizije) $\approx 10^{-3}$ s
- ako promijenimo V ili T plina → t-din. ravnot. narušena i uspostavlja se novo ravnot. stanje sa novim V ili T za $\Delta t \approx 10^{-3}$ s

⇒ ako se V ili T mijenja sporije (tj. $V \to V+\Delta V$ za $\Delta t_V \approx 10^{-1}$ s ili bolje $T \to T+\Delta T$ za $\Delta t_T \approx 10^{1}$ s tada je sigurno da će cijeli plin imati dvojnaki $T+\Delta T$ mnogo puta Δt_T) plin će imati dovoljno vremena da prijeđe u novo ravnot. stanje prije nego što se promjenljivi parametar dalje promijeni

Originalno !!!

promjena T ili V dotkom vremena je dovoljno mala da za $\Delta t \approx 10^{-3}$ s je ΔT (ili ΔV) $\to 0$

$\Delta T \approx \frac{\partial T}{\partial t}\Delta t$ tj. dakle $\frac{\partial T}{\partial t} \ll$ da za $\Delta t \approx 10^{-3}$ s je $\Delta T \ll T$ ili $\frac{\Delta T}{T} \ll 1$

- za plinove u cilindru motora sa 6000 okr/min. tj. 10^2 okr/s ⇒ $\Delta t = 10^{-2}$ s karakteristična promjena volumena još uvijek je proces „kvazistacionaran"

⇒ „dovoljno sporo" mora u t-din. stoje trivijalno značenje

→ historijski t-din. nastala kao fenomenološka teorija bazirana na dva poznata principa (I & II z. t-din.) (u t-din. ravnotezi.)

- već fenomenološki pristup omogućio otkriće čitavog niza općih zakonitosti u svojstvima materije

$\star\ dF = -PdV - SdT$

$$C_p - C_V = T\left(\frac{\partial V}{\partial T}\right)_p\left(\frac{\partial P}{\partial T}\right)_V \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \quad \& \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V \Rightarrow \left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial}{\partial V}\left(T\frac{\partial S}{\partial T}\right)_V\right)_T \overset{\text{Schwarz.}}{=} T\left(\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T\right)_V = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

- sve relacije fenomenološke t-din. mijeda općenito nezavisno od konkretnih svojstava sistema (ali u t-din. ravnoteži)

Konkretna svojstva (izražena u obliku jbi. stanja, transponiranih koef., kritičnih parametara)...) ne mogu se naći u okvirima fenomenološke t-din.

ali da bi se neki račun zasnovan na t-din. mogao dovršiti neophodno je ta svojstva poznavati

3.1. Termodinamika i statistika

→ t-din.. proučava fizičke sisteme u stanju ravnoteže, a statistički sistem. se opisuju mikrokan. i kanonskim ansamblom u faznom prostora ⇒ očekujemo zakone (principi") t-din mogu se dobiti u okvirima statist. mehanike (osvjedočit ćemo se u sadržaju tih zakona i pravih informacija o sistemu)

- sistem čestica reprezentiran u faznom prostoru jednim kanonskim ansamblom utjecaj vanj. parametara (volumen sistema, $\vec{H}$, ...) na Hamiltonijan

$$\Rightarrow \quad H = H(q_1, \dots q_S, p_1, \dots p_S, a_1, a_2, \dots) \qquad S = s \cdot N$$

- pri promjenama tih parametara ("kvazistacionarna" promjena) nad sistemom vrši se izvjestan rad, koji je očito jednak povećanju njegove energije pod tim uvjetima (tj. promjene samo tih parametara)

i to sistemu se povećava energija $dH > 0$, dok dA što mi vršimo nad sistemom radi dajemo sistemu

$$dU = dQ - dA$$

(nepotpuni diferencijal)

$$dA = -(dH)_{[a]} = \sum_k -\frac{\partial H}{\partial a_k} da_k = \sum_k A_k da_k \qquad i)$$

[a] označava da se pri uzimanju diferencijala smatra da se mijenjaju samo vanjski parametri

$$A_k = -\frac{\partial H}{\partial a_k}$$

- ima značenje generalizirane sile za odgovarajući vanjski parametar

napomena iz Kod V. S. ips generalizirana sila je $\left(-\frac{\partial H}{\partial a_k}\right)$

za neke promjene energije jedna toplina, koju je sistem u kontaktu s termostatom

$$\frac{dH}{dt} = \frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t} \neq 0$$

znači da se je $\vec{t}$ uvijek explicitno preko $a_1, a_2, \dots$

→ - veza između termodin. i statist. bazirano na kanonskom ansamblu sadržana je u:

Modul kanonske raspodjele θ. i parametar ψ ($= -\theta \ln Z$) imaju iste osobine kao apsolutna temp. T i slobodna energija F respektivno, u termodin.

Dokaz: $\theta \leftrightarrow T$

a) Ako se dovedu u termički kontakt dva ravnotežna sistema jednakih temperatura T, formirani sistem će biti također ravnotežni, i to na istom temp. T.
0 z.t.d. → Ako su pak temp. sistema dovedenih u term. kontakt bile različite kao rezultat se dobiva sistem koji nije u ravnoteži.

b) faktor $\frac{1}{T}$ je integracioni faktor za linearnu diferencijalnu formu

$$dU - \sum_k \Lambda_k da_k$$ (ima smisla o dovedenoj toplini)

II z.t.d. →

$$\frac{dU + \sum_k \Lambda_k da_k}{T} \geq dS$$

za REV tj. kvazistatički normalni, prosti

I z.t.d. $dU + d'A = d'Q = TdS$ (Kao V. Sup.) tj. $d'A = \sum_k \Lambda_k da_k$

U - unut. energija
Λ_k - intenzivni parametri koji odgovaraju koordinatama
a_k - kao ekstenzivnim parametrima

→ da li se θ tako ponaša

Dokaz a)

sistemi Σ_1 & Σ_2 u kontaktu s termostatom T_1 & T_2

$\int_{(E)} W(E)\,dE = 1$

→ gustoće vjerojatnosti zadanih vrijednosti E_1 & E_2

$$W(E_1) = \frac{1}{N_1! h^{s_1}} \frac{1}{Z_1} e^{-\frac{E_1}{\theta_1}} \Omega_1(E_1) \qquad W(E_2) = \frac{1}{N_2! h^{s_2}} \frac{1}{Z_2} e^{-\frac{E_2}{\theta_2}} \Omega_2(E_2)$$

sistame odvojimo od termostata → gustoće vjerojatnosti ostaju nepromijenjene
i dovedimo ih u međusobni kontakt pretpostavljajući prvotno da je energija (jer nema nikakvog utjecaja za promjenu)
njihove interakcije E_{12} znatno manja od njihovih vlastitih energija E_1 & E_2
(da pretp. se uvijek uvodi kod termodin. sistema) - na str. 23. → $E = E_1 + E_2$

- za novoformirani sistem

$E = E_1 + E_2$

$$W(E) = W(E_1, E_2) = W(E_1) \cdot W(E_2) = \frac{1}{N_1! N_2! h^{s_1+s_2}} \frac{1}{Z_1 \cdot Z_2} e^{-\left(\frac{E_1}{\theta_1} + \frac{E_2}{\theta_2}\right)} \Omega_1(E_1)\Omega_2(E_2) \quad (*)$$

→ što će predstavljati Kanonsku raspodjelu (tj. odgovarati sistemu u ravnoteži) jedino u slučaju kada je $\theta_1 = \theta_2$

→ ako je $\theta_1 \neq \theta_2$ (*) ne daje Kanonsku raspodjelu za energiju $E = E_1 + E_2$ ni pod kojim uvjetima

Dokaz b)

$\frac{1}{\theta}$ je integracioni faktor za lin. dif. formu

$$d\bar{E} + \sum_k \bar{A}_k da_k + d\bar{A}$$

i) $\bar{E}$ - srednja energija sistema (usrednjena po kanonskom ansamblu)
zbog male fluktuacije $\frac{\Delta E}{\bar{E}} \approx \frac{1}{\sqrt{N}}$ to je upravo unutr. energija U u termodin. smislu

$\bar{A}_k = -\overline{\frac{\partial H}{\partial a_k}}$ - usrednjeno opet po kanonskom ansamblu

$d\bar{A} = \overline{dA} = \sum_k \bar{A}_k \cdot d\overline{a_k} = \sum_k \bar{A}_k da_k$ jer $\overline{da_k} = d\bar{a}_k = da_k$ budući usrednjav. vanj. parametra po čitavom ansamblu

to je ustvari usrednjavanje Hamiltonijana po kanon. ansamblu

nigde se ne pretpostavlja da je on neovisan o sistemu, dakle za $\frac{\partial H}{\partial a_k}$ se to ne može reći, jer H ovisi o sistemu

napomena: pogledaj papir (6)

$$dW = \frac{1}{N!h^s} e^{\frac{1}{\theta}[\psi - H(q_1, \dots p_s, a)]} d\phi$$

$a = [a_1, a_2, \dots]$

$\psi = -\theta \ln Z = \psi(\theta, a)$ jer $Z = \frac{1}{N!h^s} \int_\Gamma e^{-\frac{1}{\theta} H(q_1, \dots p_s, a)} d\phi$

$\int_\Gamma dW = 1$

$$\rightarrow \int_\Gamma e^{\frac{1}{\theta}[\psi(\theta,a) - H(q_1, \dots p_s, a)]} d\phi = N! h^s \quad / \frac{\partial}{\partial a_k}$$

$$\frac{1}{\theta} \int_\Gamma \left[\left(\frac{\partial \psi}{\partial a_k}\right)_\theta - \frac{\partial H}{\partial a_k} \right] e^{\frac{\psi - H}{\theta}} d\phi = 0 \quad / \cdot \theta$$

$$\frac{1}{N!h^s} \int_\Gamma \left(\frac{\partial \psi}{\partial a_k}\right)_\theta e^{\frac{\psi - H}{\theta}} d\phi = \frac{1}{N!h^s} \int_\Gamma \frac{\partial H}{\partial a_k} e^{\frac{\psi - H}{\theta}} d\phi$$

$$\left(\frac{\partial \psi}{\partial a_k}\right)_\theta = \overline{\frac{\partial H}{\partial a_k}} = -\bar{A}_k \quad \text{(i)}$$

($\overline{\frac{\partial H}{\partial a_k}}$ - usrednj. po kan. ansamblu; $-\bar{A}_k$ kao v. sl. gore)

$$\int_\Gamma e^{\frac{\psi - H}{\theta}} \left[-\frac{1}{\theta^2}\psi + \frac{1}{\theta}\left(\frac{\partial \psi}{\partial \theta}\right)_a + \frac{1}{\theta^2} H - \frac{1}{\theta}\left(\frac{\partial H}{\partial \theta}\right) \right] d\phi = 0$$

$\left(\frac{\partial \psi}{\partial \theta}\right)_a$ i $\frac{\partial H}{\partial \theta}$ su 0

$$\frac{1}{\theta^2} \int_\Gamma \left[\theta \left(\frac{\partial \psi}{\partial \theta}\right)_a - (\psi - H)\right] e^{\frac{\psi - H}{\theta}} d\phi = 0 \quad / \cdot \theta^2$$

$$\frac{1}{N!h^s} \int_\Gamma H(q_1, \dots p_s, a) e^{\frac{\psi - H}{\theta}} d\phi = -\theta \left(\frac{\partial \psi}{\partial \theta}\right)_a \frac{1}{N!h^s} \int_\Gamma e^{\frac{\psi - H}{\theta}} d\phi + \psi \frac{1}{N!h^s} \int_\Gamma e^{\frac{\psi - H}{\theta}} d\phi$$

$$\overline{H(q_1, \dots p_s, a)} = \psi(\theta, a) - \theta \left(\frac{\partial \psi(\theta,a)}{\partial \theta}\right)_a \quad \text{(ii)}$$

→ uz parcijalne derivacije naznačeno je koje veličine su pri deriviranju smatrane konstantnim
- ovakva notacija je tradicionalna u fenomenološkoj termodinamici

uz 24 b) $H=E$ (*)

$d\bar{E} - d\bar{A} =$

$= \overline{dQ}$

$d\bar{A} = q dV$ ne $= d^{=d_{[a]}}$ - neperturb. dif. (samo po $q_1, q_2, \ldots$

— sr. vrijednost samo po $p_1, \ldots p_3$

$\Rightarrow d\bar{A} = \overline{dA}$

$dW = W(p_1, \ldots p_3, a)\, d\phi$, $a = [a_1, a_2, \ldots]$

$d\bar{A} = d \int_\Gamma A(p_1, \ldots p_3, q_1, q_2, \ldots)\, dW =$

$= \int_\Gamma dA(p_1, \ldots p_3, q_1, q_2, \ldots)\, W(p_1, \ldots p_3, a)\, d\phi$

$dW = \dfrac{e^{-\frac{1}{\Theta} H(p_1, \ldots p_3, a)}\, d\phi}{\int_\Gamma e^{-\frac{1}{\Theta} H(p_1, \ldots p_3, a)}\, d\phi}$

$= \int_\Gamma d_{[a]} A(p_1, \ldots p_3, a)\, dW$

$= \overline{d_{[a]} A}$

(?) → vjerojatno dW priroda ovisnosti: H o $a = [a_1, a_2, \ldots]$

tako da dW ne ovisi o a (*)

$\Rightarrow d_{[a]} dW = 0$ tj. $d_{[a]} W = 0$ & $d_{[a]} d\phi = 0$ očito

$\Rightarrow d_{[a]} \bar{A} = \overline{d_{[a]} A}$

$\overline{d_{[a]} A} = -\overline{(dH)_{[a]}} = +\sum_K \overline{A_K(p_1, \ldots p_3, q_1, q_2, \ldots)} \cdot da_K =$

$= +\sum_K \int_\Gamma A_K(p_1, \ldots p_3, q_1, q_2, \ldots)\, da_K \cdot dW = \sum_K da_K \int_\Gamma A_K dW$

$= \sum_K \bar{A}_K\, da_K$

(?)

$$W = \frac{e^{-\frac{1}{\theta} H(q_1 \cdots p_s, a)}}{\int_\Gamma e^{-\frac{1}{\theta} H(q_1 \cdots p_s, a)} dp}$$

$$\frac{\partial W}{\partial a} \overset{?}{=} 0$$

(24) c)

$$d\psi(\theta,a) = \left(\frac{\partial\psi}{\partial\theta}\right)_a d\theta + \sum_k \left(\frac{\partial\psi}{\partial a_k}\right)_\theta da_k$$

tot. diferencijal

$$d\left[-\left(\frac{\partial\psi}{\partial\theta}\right)_a\right] \overset{(ii')}{=} d\left(\frac{\bar{H}-\psi}{\theta}\right) = -\frac{1}{\theta^2}(\bar{H}-\psi)d\theta + \frac{1}{\theta}[d\bar{H} - d\psi]$$

$$= \frac{1}{\theta}\left[d\bar{H} - \left(\frac{\partial\psi}{\partial\theta}\right)_a d\theta - \sum_k \left(\frac{\partial\psi}{\partial a_k}\right)_\theta da_k - \frac{1}{\theta}(\bar{H}-\psi)d\theta\right] \overset{(iii)}{=}$$

$$-\left(\frac{\partial\psi}{\partial\theta}\right)_a = \frac{\bar{H}-\psi}{\theta}$$

$$= \frac{1}{\theta}\left[d\bar{H} - \sum_k \left(\frac{\partial\psi}{\partial a_k}\right)_\theta da_k\right] \overset{(i)}{=}$$

$$\left(\frac{\partial\psi}{\partial a_k}\right)_\theta = \frac{\partial\bar{H}}{\partial a_k} = -\bar{A}_k \quad \text{gen. sila}$$

$$= \frac{1}{\theta}\left[d\bar{H} + \sum_k \bar{A}_k da_k\right] \quad i')$$

$dU + d'A = d'Q = TdS$

$\Rightarrow$ desna strana totalni diferencijal

$d'A = -[dH]_{[a]}$

$H(\theta_1, p_s, a) = E \Rightarrow \bar{E} = \bar{H} \quad \& \quad \bar{E} = U$

$$\Rightarrow (*) \quad \frac{d\bar{H} + \sum_k \bar{A}_k da_k}{\theta} = \frac{d\bar{E} + \sum_k \bar{A}_k da_k}{\theta} = \frac{dU + \sum_k \bar{A}_k da_k}{\theta} \quad \text{(uzeraly preko kan. ansambla)} \quad \Leftrightarrow \quad \frac{dU + \sum_k A_k da_k}{T} = dS \qquad d'A$$

$\Rightarrow$ buduć. tin. dif. forma (*) ima isti smisao u adijabatskoj statističkoj teoriji kao i u termodinamici zaključujemo da mora biti:

$$TdS = \overset{\chi\cdot T}{\theta} d\left[-\left(\frac{\partial\psi}{\partial\theta}\right)_a\right]$$

$$\Rightarrow \quad \theta = \chi \cdot T \qquad S = -\chi\left(\frac{\partial\psi}{\partial\theta}\right)_a \quad ii')$$

χ - univerzalna konstanta, jer sistemi različite fizičke prirode u kontaktu sa istim termostatom imaju jednake module raspodjele

(* jer ako bi bilo $\theta_1 \neq \theta_2$ sistem sastavljen od (1) & (2) ne bi za energiju $E = E_1 + E_2 + \underbrace{E_{12}}_{\approx 0}$ mogao preko θ_1 & θ_2 imati neku kan. raspodjelu (tj. odgovarati sistemu u ravnotež.) što je kontradikcija sa uzetom pretp. o istom termostatu

$\Rightarrow$ numerička ireverzibilnost nastaje pri prom. kan. fiz. sistema sa poznatim osobinama

i) & ii) $\Rightarrow$ prepoznajemo I & II zakon (princip) t-dinamike

Zapravo samo II, jer smo zakon o održanju energije iskoristili još prije dobivanja ii) kod i).

(*

Dokaz: $\psi \leftrightarrow F$

$$(ii) \Rightarrow \quad \psi(\theta,a) = \bar{H}_{(\theta_1,\ldots,p_s,a)} + \theta\left(\frac{\partial\psi}{\partial\theta}\right)_a \overset{ii)}{=} \bar{E} - TS = F$$

$-\chi$, $\frac{1}{\chi}$, i) U

t-din. def. slob. energije

ili (ii) $\Rightarrow S = -\chi\left(\frac{\partial\psi}{\partial\theta}\right)_a \overset{=}{} -\left(\frac{\partial\psi}{\partial T}\right)_a$

t-din $S = -\left(\frac{\partial F}{\partial T}\right)_V$

$\Rightarrow \quad \psi \equiv F$

t-dim. Gibbs-Helmholtz jba: $U = F - T\left(\frac{\partial F}{\partial T}\right)_V$ & $H = G - T\left(\frac{\partial G}{\partial T}\right)_p$

⇒ (ii) Gibbs-Helmholtz-ova jba termodinamike

$\bar{H} = \psi - \theta\left(\frac{\partial \psi}{\partial \theta}\right)_a$

izraz za S

$$dW = \frac{e^{\frac{\psi - H}{\theta}} d\phi}{\int_\Gamma e^{\frac{\psi - H}{\theta}} d\phi}$$

$$S = -\chi \left(\frac{\partial \psi}{\partial \theta}\right)_a \overset{(ii)}{=} -\chi \frac{\psi - \bar{H}}{\theta} = -\chi \frac{\psi \int_\Gamma dW - \int_\Gamma H\, dW}{\theta} = -\chi \int_\Gamma \frac{\psi - H}{\theta} dW$$

$$= -\chi \frac{\int_\Gamma \frac{\psi - H}{\theta} e^{\frac{\psi - H}{\theta}} d\phi}{\int_\Gamma e^{\frac{\psi - H}{\theta}} d\phi}$$

$$W(q_1, \dots p_s, a) = \frac{1}{N! h^s} e^{\frac{1}{\theta}[\psi(\theta, a) - H(q_1, \dots p_s, a)]}$$

$$\Rightarrow \ln W = \frac{\psi - H}{\theta} - \ln N! h^s$$

$$\Rightarrow S = -\chi \frac{\int_\Gamma (\ln W + \ln N! h^s) e^{\frac{\psi - H}{\theta}} d\phi}{\int_\Gamma e^{\frac{\psi - H}{\theta}} d\phi} = -\chi \overline{\ln W} - \chi \ln N! h^s$$

$\left(\frac{N}{e}\right)^N$

$$S = -\chi \left(\overline{\ln W} + \ln N! h^s\right) = -\chi \left(\overline{\ln W} + \ln h^s + N \ln N - N\right)$$

$$= +\chi \cdot N - \chi N \ln N - \chi \left(\overline{\ln W} + \ln h^s\right) \quad *)$$

- sa točnošću do jedne aditivne konstante S je prop. srednjoj vrijednosti logaritma fazne gustoće vjerojatnosti i ne predstavlja srednju vrijednost neke mehaničke veličine

kao i T, S je veličina koja karakterizira cijeli stat. ansambl (a ne odnosi se na pojedina mikrostanja)

*) ⇒ S nije prop. količini tvari zbog prisustva $\ln N$, što se protivi općenitim fizičkim predodžbama

Pogreška leži u klasičnom izbrojavanju stanja

pogledaj Q.M. Kraj Ch VIII

25.2.79.

$Z = e^{-\frac{\psi}{\theta}}$ $\psi(\theta, a)$ (3.3)

3.2. Izračunavanje termodin. fja.

sa fizičkog stanovišta ima prioritet izraz $dW = \frac{1}{N! h^s} \cdot \frac{1}{Z} e^{-\frac{1}{\theta} H(q_1, \dots p_s, a)} d\phi$ $\theta = \chi T$

$Z(\theta, a)$

$\int_\Gamma dW = 1 \Rightarrow$ $Z(T,a) = \frac{1}{N! h^s} \int_\Gamma e^{-\frac{1}{\chi T} H(q_1, \dots p_s, a)} d\phi$ **statistička suma sistema**

$\psi_{(\theta,a)} = -\theta \ln Z$ $\quad S = -\chi \left(\frac{\partial \psi}{\partial \theta}\right)_a$

$\Rightarrow$ $F(T,a) = -\chi T \ln Z$ $\quad S(T,a) = -\left(\frac{\partial F}{\partial T}\right)_a$ $\quad S = -\left(\frac{\partial F}{\partial T}\right)_V$

$a = [a_1, a_2, \dots] \equiv [V, a']$ $\quad P = -\left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial U}{\partial V}\right)_S$

→ zbog i) na (24 d) $U = \bar{E}$ - preko Γ $= -\frac{1}{Z} \frac{\partial Z}{\partial (\frac{1}{\theta})}$ sa (22 c) $dW = \frac{1}{N! h^s} \cdot \frac{1}{Z} e^{-\frac{E}{\theta}} \Omega(E,a) dE$

$\theta = \chi \cdot T \Rightarrow \frac{\partial}{\partial (\frac{1}{\theta})} = -\chi T^2 \frac{\partial}{\partial T}$ $\quad \int_{(E)} dW = 1 \Rightarrow Z = \frac{1}{N! h^s} \int_{(E)} e^{-\frac{E}{\theta}} \Omega(E,a) dE$

$\Rightarrow$ $U(T,a) = -\frac{1}{Z} \frac{\partial Z}{\partial (\frac{1}{\theta})_a} = \chi T^2 \left(\frac{\partial \ln Z}{\partial T}\right)_a$ i.i. $U = F + TS$ str. 24 c)

Kaloriona jba. stanja

$U(T,a) = -\chi T \ln Z + T\left\{-\left(\frac{\partial (-\chi T \ln Z)}{\partial T}\right)_a\right\}$

$= -\chi T \ln Z + T\left\{-\chi \ln Z - \chi T \left(\frac{\partial \ln Z}{\partial T}\right)_a\right\}$

$= \chi T^2 \left(\frac{\partial \ln Z}{\partial T}\right)_a$

→ $a \equiv [a_1, a_2, \dots] \equiv [V, a']$

$dU = d'Q - d'A$ $\quad d'A = -(d\bar{H})_{[a]}^{\text{pol}} = -(d\bar{H})_{[a]} = \sum_k -\frac{\partial \bar{H}}{\partial a_k} \cdot da_k = \sum_k \bar{A}_k da_k$

opć. izrazi dif.

primjer $d'A = P dV$ $\Rightarrow$ **P je generaliz. sila** **za generaliz. koord. V**

ili $-P$ jer je rad $d'A = PdV$, ali $-PdV$ + V A dobivamo rad ($d'A > 0$)

(24 b) (i) $\Rightarrow$ $\bar{A}_k = -\frac{\partial \bar{H}}{\partial a_k} = -\left(\frac{\partial \psi}{\partial a_k}\right)_\theta$ $\Rightarrow P = -\left(\frac{\partial F}{\partial V}\right)_{T,a'}$

$P_{(T,V,a')} = -\left(\frac{\partial F_{(T,a)}}{\partial V}\right)_{T,a'}$ $\quad [T,a] = [T,V,a']$

termička jba. stanja - prema terminologiji u t-din.

lako izračunano i: $H = U + PV$ entalpija

$G = H - TS$ slobodna entalpija, Gibbsova fja, termodin. potencijal

→ **za izračunavanje svih t-din. fja. potrebno je poznavati jedino stat. sumu sistema Z**

za izračunavanje Z potrebno znati: H sistema prom. čestica, tj. u klasičnoj liniji dio interakcije među njima

u stat-termodin. se smatra da je tip interakcije unaprijed zadan, a jke. stanja se nalaze na osnovu toga, dok u fenomenološkoj t-din. se unaprijed zadaju jke. stanja

→ interakcija među česticama uslovljena je njihovom unutr. strukturom i proučavat će kvantna mehanika

3.3. Idealni plin sa translatornim stupnjevima slobode

- interakcija među molekulama zanemarena
- zanemarimo dimenzije molekula (mater. točke klas. meh.) $\Rightarrow S = 3 \cdot N$

razmatramo jednostavniji historijski model takvog plina

- relevantno jedino transl. gibanje

Složeniji (realniji) model idealnog plina uzima u obzir konačnost molek. dimenzija i time dopušta mogućnost intramolek. gibanja

izvan polja vanjskih sila

$$\Rightarrow H(q_1, \dots q_{3N}, p_1, \dots p_{3N}) = \frac{\sum_{i=1}^{3N} p_i^2}{2m}$$

m - masa molek.

$A = [V, A']$

H - ne ovisi niti o vanj. parametrima (jer ih ili nema kao $\vec{H}$ ili zbog formule idealnog plina, ne može ovisiti o V)

$$\Rightarrow Z(T) = \frac{1}{N!\,h^{3N}} \iint_{\Gamma(6N)} \dots \int e^{-\frac{1}{\chi T} \cdot \sum_{i=1}^{3N} \frac{p_i^2}{2m}} dq_1 \dots dq_{3N}\, dp_1 \dots dp_{3N}$$

$\rightarrow$ integraciju po koordinatama treba vršiti po volumenu V kojim se molekula može kretati

originalno!!!

napomena: pokušaj vršiti integraciju po Γ, ali preko H izraziti ovisnost izraza iz $\vec{V}$ preko δ-fje. itd. preko E_{pot}.

za konz. sile & klas. mehi. $H = E_{kin} + E_{pot}$ ($T+U$)

$$\Rightarrow H = \frac{1}{2m} \sum_{i=1}^{3N} p_i^2 + E_{pot}(q_1, \dots q_{3N})$$

$$E_{pot}(q_1, \dots q_{3N}) = \begin{cases} \infty & \text{izvan } V \\ 0 & \text{unutar } V \end{cases}$$

$$= E_{pot}(q_1, q_2, q_3) + \dots + E_{pot}(q_{3n-2}, q_{3n-1}, q_{3N})$$

bolje $E_{pot}(\underbrace{q_{3i-2}, q_{3i-1}, q_{3i}}_{\vec{r}_i}) = \begin{cases} \infty & \vec{r}_i \notin V \\ 0 & \vec{r}_i \in V \end{cases}$

$3 < 3i \leq 3N$

$\vec{r}_i$ - radij vektor i-te molekule

bolje zbog Jacobiana !!!

$k \cdot V = \iiint_{\Gamma \to V} dq_1 dq_2 dq_3 \quad \dots \quad V = \iiint_{\Gamma \to V} dq_{3N-2}\, dq_{3N-1}\, dq_{3N}$

$\Downarrow$

$$\iiint_{\Gamma} e^{-E_{pot}(q_{3i-2}, q_{3i-1}, q_{3i})} dq_{3i-2}\, dq_{3i-1}\, dq_{3i} = \iiint_{V} dq_{3i-2}\, dq_{3i-1}\, dq_{3i} = V$$

$\rightarrow$ naime: $k \neq 1$ ako su $q_1, q_2, \dots$ generaliz. koord. (a ne strane xyz koordinate)

$k = 1$ jer su $(q_1, q_2, \dots)$ ustvari kartezijeve prave prost. koord.

$$\Rightarrow Z = \frac{V^N}{N!\,h^{3N}} \prod_{i=1}^{3N} \int_{-\infty}^{\infty} e^{-\frac{p_i^2}{2m\chi T}} dp_i = \frac{V^N}{N!\,h^{3N}} \left[\int_{-\infty}^{+\infty} e^{-\frac{p^2}{2m\chi T}} dp \right]^{3N}$$

Poisson-ov integral

$$\int_{-\infty}^{\infty} e^{-\lambda x^2} dx = \sqrt{\frac{\pi}{\lambda}}$$

$\sqrt{\lambda}\, x = u \Rightarrow dx = \frac{du}{\sqrt{\lambda}}$

$$\int_{-\infty}^{\infty} e^{-\lambda x^2} dx = \frac{1}{\sqrt{\lambda}} \int_{-\infty}^{\infty} e^{-u^2} du = \sqrt{\frac{\pi}{\lambda}}$$

$$\Rightarrow Z_{(T,V)} = \frac{V^N}{N!\,h^{3N}} (2\pi m \chi T)^{\frac{3N}{2}} = \frac{1}{N!} \left[V \left(\frac{2\pi m \chi T}{h^2} \right)^{3/2} \right]^N$$

$$= \left[V \cdot e \cdot \frac{(2\pi m \chi T)^{3/2}}{N \cdot h^3} \right]^N$$

uvjet primjenjivosti klas. stat. fizike $\frac{V (m \chi T)^{3/2}}{h^3 N} \gg 1$

(24) el

$$\ln Z = -\ln N! + N\ln V + \frac{3}{2}N\left[\ln T + \ln \frac{2\pi m\varkappa}{h^2}\right] \qquad N! \approx \left(\frac{N}{e}\right)^N$$

$$U_{(T,V)} = \varkappa T^2 \left(\frac{\partial \ln Z}{\partial T}\right)_V = \varkappa T^2 \cdot \frac{3}{2}N \cdot \frac{1}{T} = \frac{3}{2}N\varkappa T \quad \Rightarrow U(T) \text{ za idealni plin}$$

Kalorična jba. stanja za idealni plin

$$F_{(T,V)} = -\varkappa T \ln Z = -\varkappa T \ln \frac{1}{N!}\left[V\left(\frac{2\pi m\varkappa T}{h^2}\right)^{3/2}\right]^N = -\varkappa T \ln \left[\frac{eV}{N}\left(\frac{2\pi m\varkappa T}{h^2}\right)^{3/2}\right]^N$$

$$= -N\varkappa T \ln\left[\frac{eV}{N}\left(\frac{2\pi m\varkappa T}{h^2}\right)^{3/2}\right]$$

$$S_{(T,V)} = -\left(\frac{\partial F}{\partial T}\right)_V \overset{\text{ea}}{=} N\varkappa \ln\left[\frac{eV}{N}\left(\frac{2\pi m\varkappa T}{h^2}\right)^{3/2}\right] + N\varkappa T \cdot \frac{N}{eV}\left(\frac{h^2}{2\pi m\varkappa T}\right)^{3/2} \cdot \frac{eV}{N}\left(\frac{2\pi m\varkappa}{h^2}\right)^{3/2} \cdot \frac{3}{2}T^{1/2}$$

$$= \frac{3}{2}N\varkappa + N\varkappa \ln\left[\frac{eV}{N}\left(\frac{2\pi m\varkappa T}{h^2}\right)^{3/2}\right]$$

$$P_{(T,V)} = -\left(\frac{\partial F}{\partial V}\right)_{T,\text{ea}^0} = N\varkappa T \cdot \frac{N}{eV}\left(\frac{h^2}{2\pi m\varkappa T}\right)^{3/2} \cdot \frac{e}{N}\left(\frac{2\pi m\varkappa T}{h^2}\right)^{3/2} = \frac{N\varkappa T}{V}$$

$N = \nu \tilde{N}$ $\quad \tilde{N} = 6{,}02 \cdot 10^{23}\ \text{mol}^{-1}$

$R = 1{,}98\ \text{cal/mol}\,^\circ\text{K}$

$$\left.\begin{aligned} PV &= \nu\tilde{N}\varkappa T \\ PV &= \nu R T \end{aligned}\right\} \Rightarrow \varkappa = \frac{R}{\tilde{N}} = 1{,}38 \cdot 10^{-16}\ \text{erg}/^\circ\text{K}$$

$$\varrho(H) = A e^{\frac{\Psi - H}{\Theta}} \qquad \int_\Gamma d\mathcal{W} = 1$$

$$A \int_\Gamma e^{\frac{\Psi-H}{\Theta}} d\phi = 1 \;/\cdot d[a] \qquad \Psi(\Theta, a) = -\Theta \ln Z \qquad H(q_1, \dots p_3, a) \qquad a \equiv [V, a'] \equiv [r_1, r_2, \dots]$$

mijenjamo sve veličine. Koje karakterizira sustav Θ, r_i $(\forall i)$ $\Rightarrow$ mijenjaju se Ψ i H

(*) diferenciramo postupno, ali ne po Kanon. varijablama, jer nisu od interesa za makroskop. svojstva sustava, pa se zbog toga po njima samo usrednjuju

$$\to \varrho(\Psi, \Theta, H) \Rightarrow \int_\Gamma \varrho(\Psi, \Theta, H)\, d\phi = 1 \qquad \& \text{ Liouvillov tm. } \frac{d\varrho}{dt} = 0, \quad \frac{\partial \varrho}{\partial t} = 0 \Rightarrow 0 = d\varrho = \frac{\partial \varrho}{\partial \Psi} d\Psi + \frac{\partial \varrho}{\partial \Theta} d\Theta + \frac{\partial \varrho}{\partial H} dH$$

$$dH = \underbrace{\sum_i \frac{\partial H}{\partial r_i} dr_i}_{(dH)_{[a]}} + \sum_{i=1}^{s} \left(\frac{\partial H}{\partial q_i} dq_i + \frac{\partial H}{\partial p_i} dp_i \right)$$

$$A \int_\Gamma e^{\frac{\Psi-H}{\Theta}} \left(\frac{d\Psi}{\Theta} - \frac{\Psi - H}{\Theta^2} d\Theta - \frac{1}{\Theta} \sum_i \frac{\partial H}{\partial r_i} dr_i \right) d\phi = 0 \;/\cdot \Theta$$

$A e^{\frac{\Psi}{\Theta}} = A \cdot \frac{1}{Z} = \frac{1}{\int_\Gamma e^{-\frac{H}{\Theta}} d\phi}$

$$A \int_\Gamma e^{\frac{\Psi-H}{\Theta}} \left(d\Psi_{(\Theta, a)} - \frac{\Psi - H}{\Theta} d\Theta + \sum_i \underbrace{\left(-\frac{\partial H}{\partial r_i} \right)}_{= \bar{R}_i(q_1, \dots p_3, a)} dr_i \right) d\phi = 0$$

$$d\Psi \int_\Gamma A e^{\frac{\Psi-H}{\Theta}} d\phi - \frac{\Psi}{\Theta} d\Theta \int_\Gamma A e^{\frac{\Psi-H}{\Theta}} d\phi + \frac{1}{\Theta} d\Theta \int_\Gamma H A e^{\frac{\Psi-H}{\Theta}} d\phi + \sum_i dr_i \int_\Gamma \left(-\frac{\partial H}{\partial r_i} \right) A e^{\frac{\Psi-H}{\Theta}} d\phi = 0$$

$$d\Psi - \frac{\Psi - \bar{H}}{\Theta} d\Theta + \sum_i \bar{R}_i\, dr_i = 0$$

$H(q_1, \dots p_3, a) = E \Rightarrow \bar{H} = \bar{E} = \bar{U} = U$ ← zbog malih fluktuacija

$$d\Psi = \frac{\Psi - \bar{U}}{\Theta} d\Theta - \sum_i \bar{R}_i\, dr_i \qquad (i)$$

dif. veličine koju želimo fizikalno interpretirati

t-dinamika:

$dU = T dS - \sum_i R_i\, dr_i$ unutarnja slob. energija $F = U - TS$

$$dF = dU - T dS - S dT = -S dT - \sum_i R_i\, dr_i$$

$$\Rightarrow dF = \frac{F - U}{T} dT - \sum_i R_i\, dr_i \qquad (ii)$$

→ Komparirano (i) & (ii) - članove uz odgovarajuće diferencijale

exp. opažanja ← $\bar{R}_i = \bar{R}_i$ ← izračunata iz stat. ansambla

$U = \bar{U} = \bar{E}$ (22.c)

} mjerenu identificiramo sa vrijedn. izraza preko statističke

$\Rightarrow \Psi = F$

$\int \frac{d\Theta}{\Theta} = \int \frac{dT}{T}$

$\ln \Theta - \ln \chi = \ln T$

$\Theta = \chi \cdot T$

$\Rightarrow \Theta = \chi \cdot T$

Kanonsku raspodjelu pišemo:

$$\Rightarrow \varrho = A e^{\frac{\Psi - H}{\Theta}} \to \varrho = A e^{\frac{F - H}{\chi T}}$$

χ - univ. konst., karakt. kanonske raspodjele $\equiv$ Boltz. raspodj. uslučaju idealnog plina

Boltzmanova konst.

$\varrho = A e^{\frac{F-H}{\Theta}}$ $\quad A e^{\frac{F}{\chi T}} \int_\Gamma e^{-\beta H} d\phi = 1$

$$A e^{\frac{F}{\chi T}} \int_\Gamma e^{-\beta H} d\phi = 1 \qquad \beta = \frac{1}{\chi T}$$

$$\Rightarrow \quad e^{\frac{F}{\chi T}} = \frac{1}{A \int_\Gamma e^{-\beta H} d\phi} = \frac{1}{Z}$$

$$\Rightarrow \quad \underline{F = -\chi T \ln Z}$$

ista relacija kao i za Boltzman. raspodjelu

sr. vrij. energije:

$$\bar{E} = \bar{U} = \bar{H} = \frac{A \int H e^{-\beta H} d\phi}{A \int e^{-\beta H} d\phi}$$

$H(q_1, \dots p_s, V, a')$

$\beta = \frac{1}{\chi T} = \frac{1}{\Theta}$

$A = \frac{1}{N! h^s}$

$\dim A = \dim \frac{1}{\phi} \quad \phi: [A] = [\frac{1}{\phi}]$

jer $Z = A \int_\Gamma e^{-\beta H} d\phi$ ovo mora biti veličina bez dimenzije

$$\int_\Gamma H e^{-\beta H} d\phi = -\left(\frac{\partial}{\partial \beta} \int_\Gamma e^{-\beta H} d\phi \right)_{V, a' \equiv [r_i, p_i]}$$

$\Theta = \frac{1}{\beta}$

$F = \psi = -\Theta \ln Z$

$$\Rightarrow U = \bar{U} = -\left(\frac{\partial}{\partial \beta} \ln Z \right)_{V,a'} = \left(\frac{\partial \beta F}{\partial \beta} \right)_{V,a'}$$

$-\ln Z = -\beta \chi T \ln Z = \beta F$

$$\bar{R}_i = -\left(\frac{\partial \psi}{\partial r_i} \right)_{\Theta, r_1, r_2, \dots r_{i-1}, r_{i+1}, \dots} \quad \text{tj.} \quad \bar{R}_i = -\left(\frac{\partial F}{\partial r_i} \right)_{\Theta, r_j \neq r_i \ \forall j}$$

$$\Rightarrow \quad \underline{P = -\left(\frac{\partial F}{\partial V} \right)_{T,a'} = \chi T \left(\frac{\partial \ln Z}{\partial V} \right)_{T,a'}}$$

da je P baš jedna $\bar{R}_i$ pokazano na (24) dl

jbn. stanja povezuje u najjednost. slučaju P, V, T

Zakon jednake raspodjele energije

Maxw raspodj za transl. brzine $\overline{v^2} = \frac{3kT}{m} \Rightarrow \frac{\overline{p^2}}{2m} = \frac{3}{2}kT = 3\,\frac{\overline{p_x^2}}{2m}$

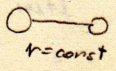
$$\Rightarrow \frac{\overline{p_x^2}}{2m} = \frac{\overline{p_y^2}}{2m} = \frac{\overline{p_z^2}}{2m} = \frac{kT}{2}$$

za idealni plin 3-st. slob x, y, z po stupnju slobode $\frac{kT}{2}$

→ srednja kin. energija za stupanj slobode ne ovisi o masi čestica

→ Poopćenje za računanje sr. kin. energ. srd.

2-A molek.



prijelaz na polarni sustav

molekula ima 3 - st. slobode $S = 3 + \underset{\text{rot.}}{3} + S_{osc.}$

S, μ - prostor

$$d\phi = dq_1 \dots dq_s\, dp_1 \dots dp_s$$

sferni (polarn.) sustav

$$dx\,dy\,dz = \frac{\partial(x,y,z)}{\partial(r,\vartheta,\varphi)}\, dr\,d\vartheta\,d\varphi$$

$$\begin{vmatrix} \cos\varphi\sin\vartheta & \sin\varphi\sin\vartheta & \cos\vartheta \\ r\cos\varphi\cos\vartheta & r\sin\varphi\cos\vartheta & -r\sin\vartheta \\ -r\sin\varphi\sin\vartheta & r\cos\varphi\sin\vartheta & 0 \end{vmatrix}$$

$x = r\cos\varphi\sin\vartheta$
$y = r\sin\varphi\sin\vartheta$
$z = r\cos\vartheta$
$\Rightarrow \frac{\partial(x,y,z)}{\partial(r,\vartheta,\varphi)} = r^2\sin\vartheta$

$$dp_x\,dp_y\,dp_z = \frac{\partial(p_x,p_y,p_z)}{\partial(p_r,p_\vartheta,p_\varphi)}\, dp_r\,dp_\vartheta\,dp_\varphi$$

$= \frac{1}{r^2\sin\vartheta}$ ako su transf. kanonske

$q_i = q_i(Q_j, P_j) \quad p_i = p_i(Q_j, P_j) \quad j = 1, \dots s$

$\Leftrightarrow \{q_i, q_j\}_{QP} = 0 \quad \{p_i, p_j\}_{QP} = 0 \quad \{q_i, p_j\}_{QP} = \delta_{ij}$

$$\vec{v} = \dot{r}\vec{r}_0 + r\dot{\vartheta}\vec{\vartheta}_0 + r\sin\vartheta\,\dot{\varphi}\,\vec{\varphi}_0 \Rightarrow L = \frac{m}{2}\vec{v}^2 + U(x,y,z) = \frac{m}{2}\left[\dot{r}^2 + r^2\dot{\vartheta}^2 + r^2\sin^2\vartheta\,\dot{\varphi}^2\right]$$

$$p_x = m\dot{x} = m\dot{r}\cos\varphi\sin\vartheta + mr\cos\varphi\cos\vartheta\,\dot{\vartheta} + mr\sin\vartheta(-\sin\varphi)\,\dot{\varphi}$$

$$\Rightarrow p_x = \cos\varphi\sin\vartheta\cdot p_r + \frac{\cos\varphi\cos\vartheta}{r}p_\vartheta - \frac{\sin\varphi}{r\sin\vartheta}p_\varphi$$

analogno

$$p_y = \sin\varphi\sin\vartheta\, p_r + \frac{\sin\varphi\cos\vartheta}{r}p_\vartheta + \frac{\cos\varphi}{r\sin\vartheta}p_\varphi$$

$$p_z = \cos\vartheta\cdot p_r - \frac{\sin\vartheta}{r}p_\vartheta + 0\cdot p_\varphi$$

$\Rightarrow p_r = \frac{\partial L}{\partial \dot{r}} = m\dot{r}$

$p_\vartheta = mr^2\dot{\vartheta}$

$p_\varphi = mr^2\sin^2\vartheta\,\dot{\varphi}$

} uopće nemaju fiz. smisla impulsa

$$\Rightarrow \frac{\partial(p_x,p_y,p_z)}{\partial(p_r,p_\vartheta,p_\varphi)} = \begin{vmatrix} \cos\varphi\sin\vartheta & \sin\varphi\sin\vartheta & \cos\vartheta \\ \frac{\cos\varphi\cos\vartheta}{r} & \frac{\sin\varphi\cos\vartheta}{r} & -\frac{\sin\vartheta}{r} \\ -\frac{\sin\varphi}{r\sin\vartheta} & \frac{\cos\varphi}{r\sin\vartheta} & 0 \end{vmatrix} = \frac{1}{r^2\sin\vartheta}$$

što je i za očekivati jer su transf. $(x,y,z,p_x,p_y,p_z) \to (r,\vartheta,\varphi,p_r,p_\vartheta,p_\varphi)$ kanonske (*)

primjer:

(*) $\{q_i, p_j\}_{QP} = \delta_{ij}$

$$\{x, p_x\}_{QP} = \left\{ \begin{array}{l} \frac{\partial x}{\partial r}\frac{\partial p_x}{\partial p_r} - \frac{\partial x}{\partial p_r}\cdot\frac{\partial p_x}{\partial r} = \cos^2\varphi\sin^2\vartheta - 0\cdot\frac{\partial p_x}{\partial r} = \cos^2\varphi\sin^2\vartheta \\ + \frac{\partial x}{\partial \vartheta}\frac{\partial p_x}{\partial p_\vartheta} - \frac{\partial x}{\partial p_\vartheta}\frac{\partial p_x}{\partial \vartheta} = r\cos\varphi\cos\vartheta\cdot\frac{\cos\varphi\cos\vartheta}{r} - 0\cdot\frac{\partial p_x}{\partial \vartheta} = \cos^2\varphi\cos^2\vartheta \\ + \frac{\partial x}{\partial \varphi}\frac{\partial p_x}{\partial p_\varphi} - \frac{\partial x}{\partial p_\varphi}\frac{\partial p_x}{\partial \varphi} = -r\sin\varphi\sin\vartheta\cdot\left(-\frac{\sin\varphi}{r\sin\vartheta}\right) - 0\cdot\frac{\partial p_x}{\partial \varphi} = +\sin^2\varphi \end{array} \right\} = 1$$

(razrad. još posebno na papiru)

(**) općenito su transformacije tog tipa kanonske $(x = x(q_1, q_2, q_3)$ itd.) gdje se K pos. lijeve izvodnice izraze za p_1, p_2, p_3 - iz jedne i druge varijable zadovoljav. Hamilt. sist.

Klas. mehanika — ukupno ima $\binom{S+2-1}{2} = \frac{(S+1)\cdot S}{2} = \frac{1}{2}S(S-1) + S$ članova (C_S^2, V_S^2) & Konz. sile $L = T - U$

$$T = E_K = \sum_{i=1}^{S}\sum_{j=1}^{S} Q_{ij}(q_1 \dots q_S)\dot{q}_i\dot{q}_j \qquad L = E_K - U(q_1, \dots q_S)$$

$$p_i = \frac{\partial E_K}{\partial \dot{q}_i}$$

$$\dot{q}_i = \frac{\partial H}{\partial p_i}$$

originalno!!! (ne vidimo značenje pot. energ. kod oscilacija)

$$\sum_{i=1}^{S}\sum_{j=1}^{S} Q_{ij}(q_1 \dots q_S)\dot{q}_i\dot{q}_j = \sum_{l\neq i=1}^{S}\sum_{j=1}^{S} Q_{ij}\dot{q}_i\dot{q}_j + \dot{q}_l\sum_{j=1}^{S} Q_{lj}\dot{q}_j =$$

$$= \sum_{l\neq i=1}^{S}\Big[Q_{il}\dot{q}_i\dot{q}_l + \sum_{l\neq j=1}^{S} Q_{ij}\dot{q}_i\dot{q}_j\Big] + \dot{q}_l^2 Q_{ll} + \dot{q}_l\sum_{l\neq j=1}^{S} Q_{lj}\dot{q}_j$$

$$= \dot{q}_l\sum_{l\neq i=1}^{S} Q_{il}\dot{q}_i + \sum_{l\neq i=1}^{S}\sum_{l\neq j=1}^{S} Q_{ij}\dot{q}_i\dot{q}_j + \dot{q}_l^2 Q_{ll} + \dot{q}_l\sum_{l\neq j=1}^{S} Q_{lj}\dot{q}_j$$

$$\Rightarrow \frac{\partial E_K}{\partial \dot{q}_l} = \sum_{l\neq i=1}^{S} Q_{il}\dot{q}_i + 2\dot{q}_l Q_{ll} + \sum_{l\neq j=1}^{S} Q_{lj}\dot{q}_j$$

$$= 2\dot{q}_l Q_{ll} + \sum_{l\neq j=1}^{S}(Q_{jl} + Q_{lj})\dot{q}_j = 2\sum_{j=1}^{S} Q_{lj}\dot{q}_j$$

ako $Q_{jl} = Q_{lj}$, a to je očito istina, jer u izrazu za E_K se umrsedavanjem dobije jednakost Q_{ij} uz jednakost $\dot{q}_i\dot{q}_j$, tj. ne $\dot{q}_j\dot{q}_i$, a da bi to mogli napisati u obliku dvostruke sume stavljamo $Q_{jl} = Q_{lj} = \frac{1}{2}Q_{jl}$

tj. ne postoje sami kombinacije s ponavljanjem $\bar{C}_n^K = \binom{n+K-1}{K}$

$$\sum_{i=1}^{S} p_i\frac{\partial H}{\partial p_i} = \sum_{i=1}^{S}\frac{\partial E_K}{\partial \dot{q}_i}\dot{q}_i = \sum_{i=1}^{S}\dot{q}_i\Big(2\sum_{j=1}^{S} Q_{ij}\dot{q}_j\Big) = 2E_K$$

$$\bar{E}_K = \frac{1}{2}\sum_{i=1}^{S}\overline{p_i\frac{\partial H}{\partial p_i}}$$

← usrednjamo preko μ-prostora po kanonskoj raspodjeli uvedenoj pod uvjetima ***) na (26) dl)

$$\overline{p_i\frac{\partial H}{\partial p_i}} = \frac{\int_\mu p_i\frac{\partial H}{\partial p_i}e^{-\beta H(q_1,\dots p_S)}d\phi_\mu}{\int_\mu e^{-\beta H}d\phi_\mu} = \frac{-\frac{1}{\beta}\int_\mu p_i\frac{\partial}{\partial p_i}e^{-\beta H}d\phi_\mu}{\int_\mu e^{-\beta H}d\phi_\mu} = -\frac{1}{\beta}\frac{\int_{\mu-p_i}\Big[\int_{p_{i\min}}^{p_{i\max}} p_i\frac{\partial}{\partial p_i}e^{-\beta H}dp_i\Big]d\phi'}{\int_\mu e^{-\beta H}d\phi}$$

dozvoljena promjena redoslijeda integracija Kanv. i izvoda

$$\int_{p_{i\min}}^{p_{i\max}} \underbrace{p_i}_{u}\underbrace{\frac{\partial}{\partial p_i}e^{-\beta H(q_1,\dots p_S)}dp_i}_{dv} = \Big[p_i\cdot e^{-\beta H(q_1,\dots p_S)}\Big]_{p_{i\min}}^{p_{i\max}} - \int_{p_{i\min}}^{p_{i\max}} e^{-\beta H(q_1,\dots p_S)}dp_i$$

$$\Big[p_i\cdot e^{-\beta H(q_1,\dots p_S)}\Big]_{p_{i\min}}^{p_{i\max}} = 0$$

sferne koordinate: $p_{i\min} = 0$, $p_{i\max} = \infty \Rightarrow H = \infty$

Kartez. koordinate: $p_{i\min} = -\infty \Rightarrow H = \sum_i \frac{p_i^2}{2m} = \infty$

$p_{i\max} = +\infty \Rightarrow H = \sum_i \frac{p_i^2}{2m} = \infty$

jer $\lim_{x\to+\infty} xe^{-x} = 0$

(27)

(2) uz (26a)

Klas. meh. & Konz. polje sila

sistem od N čestica: (nemora jednakih)

(umjesto tih N čestica (vektora) u tom 3-dim vekt. prostoru uvedimo 3N-dim Γ prostor) sa bazom $(\vec{e}_1, \dots \vec{e}_{3N})$ izgleda ustvari $\vec{e}_{3h-2} \equiv \vec{i}$ $\vec{e}_{3h-1} \equiv \vec{j}$ $\vec{e}_{3h} \equiv \vec{k}$ $\forall h = 1, \dots N$

opća sila na sistem kao 1 točka u Γ prostoru!

$$\vec{F}_c \equiv \left(\vec{F}_1 + \sum_{j=2}^{N} \vec{F}_{j1}, \dots \underbrace{\vec{F}_h + \sum_{j=1}^{N} \vec{F}_{jh}}_{\vec{F}_{h\,tot}}, \dots \vec{F}_N + \sum_{j=1}^{N} \vec{F}_{jN} \right) \quad \text{gdje } \vec{F}_{hh} = 0 \;\; \forall h = 1, \dots N$$

$$\vec{F}_c \equiv (X_1, \dots X_i, \dots X_{3N})$$

gdje $\vec{F}_{h_{x\,tot}} \equiv X_h = X_{3h-2}$ $\vec{F}_{h_{y\,tot}} = X_{3h-1}$ $\vec{F}_{h_{z\,tot}} = X_{3h}$

$$\vec{r}_c \equiv (\vec{r}_1, \dots \vec{r}_h, \dots \vec{r}_N) \equiv (X_1, \dots X_i, \dots X_{3N})$$

$$d\vec{r}_c \equiv (d\vec{r}_1, \dots d\vec{r}_h, \dots d\vec{r}_N) \equiv (dx_1, \dots dx_i, \dots dx_{3N}) = \sum_{i=1}^{3N} dx_i \cdot \vec{e}_i$$

gdje: $x_h = x_{3h-2}$ $y_h = x_{3h-1}$ $z_h = x_{3h}$

Pokazati: (Ya) ako $\vec{F}_h = -\text{grad}_h U_h(\vec{r}_h)$ ($U_h(\vec{r}_h)$)

$\vec{F}_{jh} = -\text{grad}_h U_{jh}(\vec{r}_{jh})$ ($U_{jh}(\vec{r}_{jh})$)

$\Rightarrow X_i = -\dfrac{\partial U(x_1, \dots x_{3N})}{\partial x_i}$ $\forall i = 1, \dots 3N$

gradijent u Γ-prostoru $-\text{grad}_c = -\sum_{i=1}^{3N} \vec{e}_i \dfrac{\partial}{\partial x_i}$

$\Rightarrow \vec{F}_c = -\text{grad}_c U(x_1, \dots x_{3N})$

$$\vec{F}_c \cdot d\vec{r}_c \overset{\text{opć. pod. def.}}{=} \sum_{i=1}^{3N} X_i \, dx_i = \sum_{h=1}^{N} \vec{F}_{h\,tot} \cdot d\vec{r}_h =$$

$$= \sum_{h=1}^{N} \left(\vec{F}_h + \sum_{j=1}^{N} \vec{F}_{jh} \right) d\vec{r}_h = d'R \quad \text{(i)}$$

$\vec{r}_c = \sum_{i=1}^{3N} \vec{e}_i \cdot x_i$

$d\vec{r}_c = \sum_{i=1}^{3N} \vec{e}_i \, dx_i$

Opći teorem o kinetičkoj energiji (za sustav od N čestica)

$\vec{F}_{hh} = 0 \quad \forall h$

$$\text{rad mora biti totalni diferencijal: } \quad d'R = \sum_{h=1}^{N} d'R_h = \sum_{h=1}^{N} \left(\vec{F}_h + \sum_{j=1}^{N} \vec{F}_{jh}\right) d\vec{r}_h = \sum_{h=1}^{N} \vec{F}_h \, d\vec{r}_h + \frac{1}{2} \sum_{h=1}^{N} \sum_{j=1}^{N} \vec{F}_{jh} \, d\vec{r}_{jh}$$

$$\sum_{h=1}^{N} \sum_{j=1}^{N} \vec{F}_{jh} \, d\vec{r}_h = \frac{1}{2} \sum_{h=1}^{N} \sum_{j=1}^{N} \left(\vec{F}_{jh} \, d\vec{r}_h + \vec{F}_{hj} \, d\vec{r}_j\right) = \vec{F}_{hj} = -\vec{F}_{jh} = \frac{1}{2} \sum_{j} \sum_{h} \vec{F}_{jh} \, d\vec{r}_{jh}$$

$$\sum_{h=1}^{N} \vec{F}_h \, d\vec{r}_h = -\sum_{h=1}^{N} \text{grad}_h \, U_h(\vec{r}_h) \cdot d\vec{r}_h = -\sum_{h=1}^{N} d\, U_h(\vec{r}_h) = -d \underbrace{\left(\sum_{h=1}^{N} U_h(\vec{r}_h)\right)}_{U_v(\vec{r}_c)}$$

$$\frac{1}{2} \sum_{h=1}^{N} \sum_{j=1}^{N} \vec{F}_{jh} \, d\vec{r}_{jh} = \sum_{h=1}^{N} \left(\sum_{j=1}^{N} \vec{F}_{jh}\right) d\vec{r}_h = \frac{1}{2} \sum_{h=1}^{N} \sum_{j=1}^{N} -\text{grad}_h \, U_{jh}(\vec{r}_{jh}) \, d\vec{r}_{jh} =$$

$$= -\frac{1}{2} \sum_{h=1}^{N} \sum_{j=1}^{N} S' \frac{\partial U_{jh}(x_h - x_j, y_h - y_j, z_h - z_j)}{\partial x_h} d(x_h - x_j) \quad \text{na mjestu } h\text{-tog č.}$$

$$= -\frac{1}{2} \sum_{h=1}^{N} \sum_{j=1}^{N} S' \frac{\partial U_{jh}(x_h - x_j, y_h - y_j, z_h - z_j)}{\partial (x_h - x_j)} d(x_h - x_j)$$

$$= -\frac{1}{2} \sum_{h=1}^{N} \sum_{j=1}^{N} dU_{jh} \quad \text{dodatni} \quad = -d\left(\frac{1}{2} \sum_{h=1}^{N} \sum_{j=1}^{N} U_{jh}\right)$$

nije samo $S' \frac{\partial U_{jh}}{\partial x_h} \cdot dx_h$ nego dif. per je U_{jh} još fja x_j, y_j, z_j

$$\Rightarrow d'R = -d\left[\underbrace{\sum_{h=1}^{N} U_h(\vec{r}_h)}_{U_v(\vec{r}_c)} + \frac{1}{2} \underbrace{\sum_{h=1}^{N} \sum_{j=1}^{N} U_{jh}(\vec{r}_{jh})}_{U_u(\vec{r}_c)}\right] = -d\,\underbrace{U(x_1, \ldots x_{3N})}_{U(\vec{r}_c)} \qquad (\star\star)$$

$$\Rightarrow d'R = dR$$

$$\text{(7.8) } (\star\star) \Rightarrow \sum_{i=1}^{3N} X_i \, dx_i = -d\,U(x_1, \ldots x_{3N}) \Rightarrow \underline{X_i = -\frac{\partial U(x_1, \ldots x_{3N})}{\partial x_i}}$$

gdje je $U(x_1, \ldots x_{3N}) = \sum_{h=1}^{N} U_h(\underbrace{x_{3h-2}, x_{3h-1}, x_{3h}}_{(x_h\ y_h\ z_h)}) + \frac{1}{2} \sum_{h=1}^{N} \sum_{j=1}^{N} U_{jh}(\underbrace{x_{3h-2} - x_{3j-2}, x_{3h-1} - x_{3j-1}, x_{3h} - x_{3j}}_{x_h - x_j,\ y_h - y_j,\ z_h - z_j})$

pot. energija interakcije

$\rightarrow U(x_1, \ldots x_{3N}, t)$ ako $U_h(x_{3h-2}, x_{3h-1}, x_{3h}, t)$ (i)

$S' = 3N$ tj. isključujemo rotacije i oscilacije unutar molekule $\quad 1-A$

(26) a)

Landau - Lifšic

$H = T + U$ $\quad E_k$

za Klas. meh. & Konz. sile $\quad L = T - U$

$$L = \sum_{i=1}^{3N} \frac{m_i}{2} \dot{x}_i^2 - U(x_1, \dots x_{3N})$$

N-čestica Kartezij. koordinate $x_i \quad i = 1, \dots 3N$

$\Rightarrow x_h = x_{3h-2} \quad y_h = x_{3h-1} \quad z_h = x_{3h} \quad h = 1, \dots N$

$$\vec{F}_c = -\text{grad}_c U(x_1, \dots x_{3N})$$

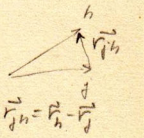
$$\Rightarrow X_i = -\frac{\partial U}{\partial x_i}$$

$$x_i = x_i(q_1, \dots q_s) \qquad \dot{x}_i = \sum_{j=1}^{s} \frac{\partial x_i}{\partial q_j} \dot{q}_j$$

$\forall i = 1, \dots 3N$ $\quad s = 3N$ ako nema ograničenja na gibanje, tada što i nema veze među sistema čestica

$$\vec{F}_h = -\text{grad}_h U_h(\vec{r}_h)$$

$$\sum_{j=1}^{N} \vec{F}_{jh} = -\text{grad}_h \sum_{\substack{j=1 \\ h \neq j}}^{N} U_{jh}(\vec{r}_{jh})$$



Ukupna sila na h-tu česticu:

$$\vec{F}_{h_{tot}} = \vec{F}_h + \sum_{j=1}^{N} \vec{F}_{jh} = -\text{grad}_h \Big[U_h(x_h, y_h, z_h) + \sum_{h \neq j=1}^{N} U_{jh}(x_h - x_j, y_h - y_j, z_h - z_j) \Big]$$

(x_h, y_h, z_h)

$$= -\text{grad}_h U_{h_{tot}}(x_1, y_1, z_1, \dots x_N, y_N, z_N)$$

gdje: $-\text{grad}_h \Rightarrow$ Sila $\dfrac{\partial}{\partial x_h}$

$$X_h = -\frac{\partial U_{h_{tot}}}{\partial x_h} \qquad Y_h = -\frac{\partial U_{h_{tot}}}{\partial y_h} \qquad Z_h = -\frac{\partial U_{h_{tot}}}{\partial z_h} \qquad h = 1, \dots N$$

(za N istovrsnih čestica dovoljno je da je $U_{h\,tot}$ isto fja (u smislu jednak fja) za $\forall$ čestica $1, \dots N$)

pogledaj (*) papir

$\forall i = 1, \dots 3N$ $\quad$ alb nema ograničenja na gibanje, tada što i nema veze među sistema čestica

$$\Rightarrow L = \frac{1}{2} \sum_{i=1}^{3N} m_i \Big(\sum_{j=1}^{s} \frac{\partial x_i}{\partial q_j} \dot{q}_j \Big)^2 - U(q_1 \dots q_s)$$

$$L = \frac{1}{2} \sum_{i=1}^{s} \sum_{j=1}^{s} a_{ij}(q_1, \dots q_s) \dot{q}_i \dot{q}_j - U(q_1, \dots q_s)$$

$\sum_{i,j=1}^{s}$

$$\Rightarrow L = \sum_{i=1}^{s} \sum_{j=1}^{s} a_{ij}(q_1, \dots q_s) \dot{q}_i \dot{q}_j - U(q_1, \dots q_s)$$

$s = 3N$ tj. isključujemo oscilacije i rotacije molekule $\quad$ 1-A molek.

(*)

§ 46. Liouville-ov teorem

- fazni prostor Γ $\quad$ $2s$-dim $\quad s = s \cdot N$

$$d\Gamma = dq_1 \dots dq_s \, dp_1 \dots dp_s$$ elem. volum. faznog prostora

$\int d\Gamma$ - ima svojstvo invarijantnosti u odnosu na kanonske transformacije

neko podr. faznog prostra

→ Kanonska transformacija: sustav invertnih fja.

(*) $\quad Q_i = Q_i(q_j, p_j) \qquad p_i = p_i(q_j, p_j) \qquad \begin{matrix} i = 1, \dots s \\ j = 1, \dots s \end{matrix}$

može još expl. t (Landau §45)

ako $\{u, v\}_{q,p} = \{u, v\}_{Q,P} \Leftrightarrow \{Q_i, Q_k\}_{Q,P} = 0$

$\Rightarrow H(q_i, p_i) = \bar{H}(Q_j, P_j)$ $\qquad \{p_i, p_k\}_{Q,P} = 0$

$$\Rightarrow \dot{Q}_j = \frac{\partial \bar{H}}{\partial P_j} = \{Q_j, \bar{H}\}_{Q,P} \qquad \dot{P}_j = -\frac{\partial \bar{H}}{\partial Q_j} = \{P_j, \bar{H}\}_{Q,P}$$

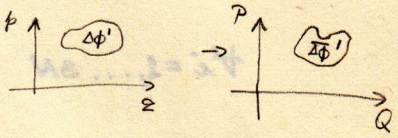
$\{q_i, p_k\}_{Q,P} = \delta_{ik}$

→ ako se izvrši kanon. transf. (*) od varijabli p, q na P, Q tada su volumeni uzajamno odgovarajućih područja prostora p, q & P, Q jednaki

$$\Delta\phi' = \int\cdots\int_{\Delta\phi} dq_1 \cdots dq_s\, dp_1 \cdots dp_s = \int\cdots\int_{\Delta\bar{\phi}} dQ_1 \cdots dQ_s\, dP_1 \cdots dP_s = \Delta\bar{\phi}' \qquad (**)$$

$\forall j$

$$1 = \lim_{\Delta\bar{\phi}' \to 0} \frac{\Delta\phi'}{\Delta\bar{\phi}'} = \frac{\partial(q_1, \ldots p_s)}{\partial(Q_1, \ldots P_s)}$$



$$\int\cdots\int dQ_1 \cdots dP_s = \int\cdots\int \mathrm{I\!I}\, dq_1 \cdots dp_s \qquad \mathrm{I\!I} = \frac{\partial(Q_1, \ldots P_s)}{\partial(q_1, \ldots p_s)}$$

Dokaz (**) se svodi na dokaz $\mathrm{I\!I} = 1$ za $\forall$ kanon. transf.

$$\mathrm{I\!I} = \frac{\partial(Q_1, \ldots Q_s, P_1, \ldots P_s)}{\partial(q_1, \ldots q_s, p_1, \ldots p_s)} = \begin{vmatrix} \frac{\partial Q_1}{\partial q_1} & \cdots & \frac{\partial Q_s}{\partial q_1} & \frac{\partial P_1}{\partial q_1} & \cdots & \frac{\partial P_s}{\partial q_1} \\ \vdots & & & & & \\ \frac{\partial Q_1}{\partial p_s} & \cdots & \frac{\partial Q_s}{\partial p_s} & \frac{\partial P_1}{\partial p_s} & \cdots & \frac{\partial P_s}{\partial p_s} \end{vmatrix} \quad (*)$$

$Q_i = Q_i(q_1, \ldots p_s, t)$
$P_i = P_i(q_1, \ldots p_s, t)$ $\quad i = 1, \ldots s$

$\phi(q_j, P_j, t)$ kan. transf. $\Rightarrow p_j = \frac{\partial\phi}{\partial q_j}$, $Q_j = \frac{\partial\phi}{\partial P_j}$.

$$(1)\begin{cases} Q_i = Q_i(q_1, \ldots q_s, p_1, \ldots p_s, t) \\ P_i = P_i(q_1, \ldots q_s, p_1, \ldots p_s, t) \end{cases} \quad i = 1, \ldots s$$

inverzija sustava fja. $\Rightarrow Q_i, P_i$ $i = 1, \ldots s$ nezav. varijable ako Jacobijan $\neq 0$ *)

$$\Rightarrow (1')\begin{cases} q_j = q_j(Q_1, \ldots Q_s, P_1, \ldots P_s, t) \\ p_j = p_j(Q_1, \ldots Q_s, P_1, \ldots P_s, t) \end{cases} \quad j = 1, \ldots s$$

$\Rightarrow$ možemo uzeti iz (1) & (1')

$$(2)\begin{cases} q_j = q_j'(q_1, \ldots q_s, P_1, \ldots P_s, t) \\ p_j = p_j'(q_1, \ldots q_s, P_1, \ldots P_s, t) \end{cases} \quad j = 1, \ldots s$$

Q_i $\forall i$ iz (1) uvrstimo u (1')

$\rightarrow p_j = p_j''(q_1, \ldots q_s, p_1, \ldots p_s, P_1, \ldots P_s, t)$ $j = 1, s$

iz dobivenog izrazimo p_j $j = 1, \ldots s$, a zatim uvrstimo u gornje relacije (1') $\Rightarrow$ (2)

$$\frac{\partial Q_i}{\partial q_j} = \sum_{k=1}^{s} \frac{\partial Q_i}{\partial q_k}\underbrace{\frac{\partial q_k}{\partial q_j}}_{\delta_{jk}} + \frac{\partial Q_i}{\partial p_k}\underbrace{\frac{\partial p_k}{\partial q_j}}_{=0}$$

$$\frac{\partial P_i}{\partial q_j} = \sum_{k=1}^{s} \frac{\partial P_i}{\partial q_k}\underbrace{\frac{\partial q_k}{\partial q_j}}_{\delta_{jk}} + \frac{\partial P_i}{\partial p_k}\underbrace{\frac{\partial p_k}{\partial q_k}}_{=0}$$

$$\frac{\partial Q_i}{\partial P_j} = \sum_{k=1}^{s} \frac{\partial Q_i}{\partial q_k}\frac{\partial q_k}{\partial P_j} + \frac{\partial Q_i}{\partial p_k}\frac{\partial p_k}{\partial P_j} \qquad i = 1, s \quad j = 1, s.$$

$$\underbrace{\frac{\partial P_i}{\partial P_j}}_{\delta_{ij}} = \sum_{k=1}^{s} \frac{\partial P_i}{\partial q_k}\frac{\partial q_k}{\partial P_j} + \frac{\partial P_i}{\partial p_k}\frac{\partial p_k}{\partial P_j} \qquad i, j = 1, \ldots s$$

Lifšic-Landau

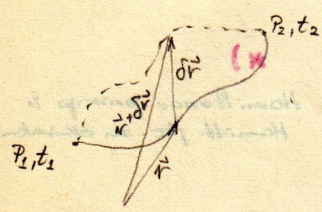
§45. Kanonske transformacije

za klas. sile: $L = \sum_{i,j} Q_{ij}(q_k)\dot{q}_i\dot{q}_j - U(q_1,\dots q_{3N})$ (1)

$h = r - s < r - (3n-\ell)$

$\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j}\right) - \frac{\partial L}{\partial q_j} = \sum_{k=1}^{h} \lambda_k a_{kj}$ $\quad j=1,\dots r$ $\quad k=1,\dots s$

za $h=0$ slob. sustav: $\frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j}\right) - \frac{\partial L}{\partial q_j} = 0$ $\quad j=1,\dots s$ (*)



$\delta \vec{r}_h\big|_{t_1} = \delta \vec{r}_h\big|_{t_2} = 0 \quad \forall h = 1,\dots N$

$\Rightarrow \delta S = 0 \quad$ tj. $\delta \int_{t_1}^{t_2} L\,dt = \int_{t_1}^{t_2} \delta L\,dt = 0$ (*) $\Rightarrow \int_{t_1}^{t_2} \sum_{j=1}^{r} \left[\frac{\partial L}{\partial q_j}\delta q_j + \frac{\partial L}{\partial \dot{q}_j}\delta \dot{q}_j\right] dt = 0$

može biti: $L(q_i, \dot{q}_i, t)$

sjetimo zamj. beznačn. varv. i vrem. deriv.: $\frac{d}{dt}\left[\frac{\partial L}{\partial \dot{q}_j}\delta q_j\right] = \frac{d}{dt}\left[\frac{\partial L}{\partial \dot{q}_j}\right]\delta q_j + \frac{\partial L}{\partial \dot{q}_j}\delta \dot{q}_j$

$\Rightarrow \frac{d}{dt}\left(\frac{\partial L}{\partial \dot{q}_j}\right) - \frac{\partial L}{\partial q_j} = \sum_{k=1}^{h} \lambda_k a_{kj}$ (1*)

Kanonske jbe! (slob. sustav) $p_j = \frac{\partial L}{\partial \dot{q}_j} \Rightarrow \dot{p}_j = \frac{\partial L}{\partial q_j} \quad j=1,\dots s$

$H = \sum_{j=1}^{s} p_j\dot{q}_j - L \quad \Rightarrow \quad \dot{q}_j = \frac{\partial H}{\partial p_j} \quad \dot{p}_j = -\frac{\partial H}{\partial q_j}$ (**) $\quad \frac{dH}{dt} = \frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t}$

$x_i = x_i(q_1,\dots q_r)$ $\quad i=1,\dots 3N$ $\quad h = r - s = r - (3n-\ell)$ (ujetja)

→ izbor general. koord. $q \equiv (q_1,\dots q_s)$ nije ograničen nikakvim ujetima & formalni oblik Lagrange-ovih jbi (*) nezavisi od tog izbora ⇒ Lagrange-ove jbe invarijante u odnosu na transform. koordinata $q_1, q_2, \dots q_s$ na ma koje druge nezavisne veličine $Q_1, Q_2, \dots Q_s$ (ili n_2)

dopuštamo: $Q_i = Q_i(q_1,\dots q_s, t)$ $\quad i=1,\dots s$ (može i neki r)

točkasta transformacija

⇒ Lagrang. jbe (*) & Hamilt. jbe (**) zadržavaju svoj oblik – jer je to samo transf. koord – a ne još generaliz. impulsa

tj. samo je drugi $x_i = \bar{x}_i(Q_1,\dots Q_r)$ $i=1,\dots 3N$

ali Hamilt. jbe (**) dopuštaju znatno širu klasu transformacija, budući impulsi p_j $(j=1,\dots s)$ igraju usporedo sa koordinatama q_j ulogu ravnopravnih nezav. varijabli

→ proširimo pojam transformacije koji će uključiti svih 2s varijabli

$pq \to PQ$

sustav invarijantnih jbi.

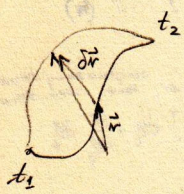
$$Q_i = Q_i(q_1,\dots p_s, t) \qquad P_i = P_i(q_1,\dots p_s, t) \qquad i = 1,\dots s$$

(**) $\quad q_i = q_i(Q_1,\dots P_s, t) \qquad p_i = p_i(Q_1,\dots P_s, t)$

→ takvo proširenje klase dozvoljenih transf. je jedna od bitnih prednosti Hamilt. metode mehanike

Uvjeti da bi jbe. gibanja sa novim varijablama P, Q imale oblik

(i) $\dot{Q}_i = \frac{\partial \bar{H}}{\partial P_i} \qquad \dot{P}_i = -\frac{\partial \bar{H}}{\partial Q_i} \qquad i = 1, \dots s$ tj. da je transformacija kanonska



$\delta \int_{t_1}^{t_2} L\,dt = 0$ $\Leftrightarrow$ (Opet mi to) $H = \sum_{j=1}^{s} p_j \dot{q}_j - L$ & $\dot{q}_j = \frac{\partial H}{\partial p_j} \quad \dot{p}_j = -\frac{\partial H}{\partial q_j}$ *)

budući se radi o točkastoj transf., kod je to trivijalno ispunjeno

tj. Hamiltonov princip & Hamilt. jbe. su ekvivalentni

(**) $\Rightarrow \quad H(q_1, \dots p_s, t) \to \bar{H}(Q_1, \dots P_s, t)$

(i) & *)

$\Rightarrow \quad \delta \int_{t_1}^{t_2} \left(\sum_{j=1}^{s} P_j\,dQ_j - \bar{H}\,dt \right) = 0$

** $\Rightarrow \quad \delta \int_{t_1}^{t_2} \left(\sum_{j=1}^{s} p_j\,dq_j - H\,dt \right) = 0$ $\Rightarrow$

$\Rightarrow \quad \delta \int_{t_1}^{t_2} \left[\left(\sum_{j=1}^{s} p_j\,dq_j - H\,dt \right) - \left(\sum_{j=1}^{s} P_j\,dQ_j - \bar{H}\,dt \right) \right] = 0$

$\delta \int_{t_1}^{t_2} F(q_j, Q_j, t) \Rightarrow$ ($\leftarrow d\vec{r} = \frac{d\vec{r}}{dt}\,dt$) $\quad \delta F(q_j, p_j, Q_j, P_j, t)\Big|_{t_1}^{t_2} = \sum_{j=1}^{s} \left(\frac{\partial F}{\partial q_j} \delta q_j + \frac{\partial F}{\partial p_j} \delta p_j + \frac{\partial F}{\partial Q_j} \delta Q_j + \frac{\partial F}{\partial P_j} \delta P_j \right)_{t_1}^{t_2} = 0$ (vezivni vanjskom $\Rightarrow \delta t = 0$)

$j = 1, \dots s$

(M)

$\delta Q_j = \sum_{i=1}^{s} \frac{\partial Q_j}{\partial q_i} \delta q_i$ & $\delta q_j|_{t_1} = \delta q_j|_{t_2} = 0$ $\quad (*)\ \delta p_j|_{t_1} = \delta p_j|_{t_2} = 0$ $\Rightarrow \quad \delta Q_j|_{t_1} = \delta Q_j|_{t_2} = 0$, $\delta P_j|_{t_1} = \delta P_j|_{t_2} = 0$

→ nepotrebno!!! (*) $\delta p_j = \delta \frac{\partial L}{\partial \dot{q}_j} = \delta f(q_1, \dots q_s, \dot{q}_1, \dots \dot{q}_s) = \sum_{j=1}^{s} \left(\frac{\partial f}{\partial q_j} \delta q_j + \frac{\partial f}{\partial \dot{q}_j} \delta \dot{q}_j \right) =$

$= \sum_{j=1}^{s} \left(\frac{\partial f}{\partial q_j} \delta q_j + \frac{\partial f}{\partial \dot{q}_j} \frac{d}{dt}(\delta q_j) \right)$ $\Rightarrow$ ako $\delta q_j|_{t_1} = 0 \ \forall j = 1, \dots s$ (i) $\Rightarrow \delta p_j|_{t_2} = 0$

(M)

$\Rightarrow \quad dF = \sum_{j=1}^{s} p_j\,dq_j - \sum_{j=1}^{s} P_j\,dQ_j + (\bar{H} - H)\,dt$

$F(q_j, p_j, Q_j, P_j, t)$

izvodna fja. transformacije kanonske

$\Rightarrow \quad \underline{p_j = \frac{\partial F}{\partial q_j}} \qquad \underline{P_j = -\frac{\partial F}{\partial Q_j}} \qquad \underline{\bar{H} = H + \frac{\partial F}{\partial t}}$

→ izrazimo novu izvodnu fju. nekako $F(q_j, Q_j, t)$ već preko $q_j, P_j, t \quad j = 1, \dots s$

$\sum_{j=1}^{s} P_j\,dQ_j = d \sum_{j=1}^{s} P_j Q_j - \sum_{j=1}^{s} Q_j\,dP_j$

$\Rightarrow \quad d\left(F + \sum_{j=1}^{s} P_j Q_j \right) = \sum_{j=1}^{s} p_j\,dq_j + \sum_{j=1}^{s} Q_j\,dP_j + (\bar{H} - H)\,dt$

$F + \sum_{j=1}^{s} P_j Q_j = \phi(q_j, P_j, t) \qquad j = 1, \dots s$

$j = 1, \dots s$

$$d\phi(q_j, P_j, t) = \sum_{j=1}^{s} p_j \, dq_j + \sum_{j=1}^{s} Q_j \, dP_j + (\bar{H} - H)\,dt$$

$\phi(q_j, P_j, t)$ $j = 1, \dots s$ — izvodna fja. za Kanon. transformaciju

$$\Rightarrow \quad p_j = \frac{\partial \phi}{\partial q_j} \qquad Q_j = \frac{\partial \phi}{\partial P_j} \qquad \bar{H} = H + \frac{\partial \phi}{\partial t} \qquad (i)$$

→ ako uzmemo $\phi(q_j, P_j, t) = \sum_{j=1}^{s} f_j(q_1, \dots q_s, t) P_j$ $\quad f_i$ – proizv. fje.

$\Rightarrow Q_j = f_j(q_1, \dots q_s, t) \quad \forall j = 1, \dots s$ $\qquad p_j = \sum_{j=1}^{s} P_j \cdot \frac{\partial f_j}{\partial q_j}$ $\quad j = 1, \dots s$ rješimo Cramerov sistem $\Rightarrow P_j(q_1, \dots f_s)$

f_j nove Koord. ovise samo o starim, ali i o impulsima $\Rightarrow$ točkasta transform.

spec. slučaj Kanonskih transformacija

→ analogno prethodno na formule Kan. transf. koje su izraž. preko izvod. fja od $(p \& Q)$ ili $(p \& P)$

međutim $\bar{H}$ uvijek dat istom relacijom

→ ako $\frac{\partial \phi}{\partial t} = 0 \Rightarrow \bar{H} = H$ (ii)

f_j: dovoljno samo urediti $q_j, p_j \ \forall j$ (i)

→ Sirina Kanon. transf. u znatnoj mjeri olakšava Hamilt. metodu pojam generaliz. Koord. i impulsa od njihovog prvobitnog smisla

→ ako $\Phi = \left(\sum_{j=1}^{s} f_j(q_j, t) P_j \right) = \sum_{j=1}^{s} q_j Q_j \quad \Rightarrow \bar{H} = H$

$\Rightarrow p_j = Q_j \qquad P_j = -q_j$ (je Kanonska)

ta transf. nemijenja eksplicitno Kan. oblik jbi. i svodi se na međusobnu zamjenu imena Koord. i impulsa

→ varijable $p_j, q_j \ \forall j$ nazivamo Kanonske konjugirane veličine

$$H = \sum_{i=1}^{s} \frac{\partial L}{\partial \dot{q}_i} \dot{q}_i - L \qquad p_i$$

gdje $L(q_j, \dot{q}_j, t)$ $\quad j = 1, \dots s$ $\quad$ za klas. meh. & Konz. sile $L = \sum_{i,j} Q_{ij}(q_k)\dot{q}_i\dot{q}_j - U(q_k, t)$ $\quad k = 1, \dots s$

$\frac{dH}{dt} = \frac{\partial H}{\partial t} = -\frac{\partial L}{\partial t}$ ako L ovisi expl. t

općenito: $H = H(q_1, \dots q_s, p_1, \dots p_s, t)$

$$\left.\begin{aligned} \dot{q}_i &= \frac{\partial H}{\partial p_i} \\ \dot{p}_i &= -\frac{\partial H}{\partial q_i} \end{aligned}\right\} \Rightarrow \left.\begin{aligned} q_{i_t} &= q_i(q_1^\circ, \dots p_s^\circ, p_1^\circ, \dots p_s^\circ, t) \\ p_{i_t} &= p_i(q_1^\circ, \dots p_s^\circ, p_1^\circ, \dots p_s^\circ, t) \end{aligned}\right\} i = 1, \dots s \quad (1)$$

gdje je $q_{i_0} = q_i^\circ \quad p_{i_0} = p_i^\circ \quad t = 0 \quad i = 1, \dots s$

$$\Rightarrow \left.\begin{aligned} q_{i_{t+\tau}} &= q_i(q_1^\circ, \dots q_s^\circ, p_1^\circ, \dots p_s^\circ, t+\tau) \\ p_{i_{t+\tau}} &= p_i(q_1^\circ, \dots q_s^\circ, p_1^\circ, \dots p_s^\circ, t+\tau) \end{aligned}\right\} (2) \quad i = 1, \dots s$$

(1) predstavlja inverziju sustava f-a. iz kojeg izrazimo q_j°, p_j° $(j = 1, \dots s)$ preko q_{i_t}, p_{i_t} $(i = 1, \dots s)$, expl. preko t, koji se uklida nakon uvrštavanja

$$\Rightarrow \left.\begin{aligned} q_{i_{t+\tau}} &= q_i'(q_{1_t}, \dots q_{s_t}, p_{1_t}, \dots p_{s_t}, \tau) \\ p_{i_{t+\tau}} &= p_i'(q_{1_t}, \dots q_{s_t}, p_{1_t}, \dots p_{s_t}, \tau) \end{aligned}\right\} i = 1, \dots s \quad (3)$$

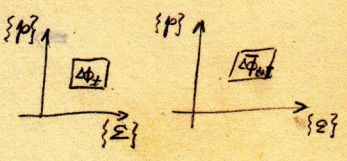
$\dot{q}_{i_t} = \left(\frac{\partial H}{\partial p_i}\right)_t$, $\dot{q}_{i_{t+\tau}} = \left(\frac{\partial H}{\partial p_i}\right)_{t+\tau}$ $\Rightarrow$ (3) je kanonska (**) transformacija gen. koordinata $\quad q_{i_t}, p_{i_t} \to q_{i_{t+\tau}}, p_{i_{t+\tau}}$ $\quad i = 1, \dots s$

→ budući (1) & (2) zadovoljavaju kanonske jdbe za t & $t+\tau$

ali bitno: u istom faznom prostoru Γ, jako da te transf. u biti predstavljaju gibanje faznih točaka (pa i onih koje leže na hiperplohi koja odrezuje volumen $\Delta\phi'$) dakle i $\Delta\phi_t \to \Delta\phi_{t+\tau}$

(*) $\Rightarrow$ $\quad \mathcal{J} = \frac{\partial(q_{1_t} \dots p_{s_t})}{\partial(q_{1_{t+\tau}} \dots p_{s_{t+\tau}})} = 1$ $\quad$ & $\quad \lim_{\Delta\phi_t' \to 0} \frac{\Delta\phi_t'}{\Delta\phi_{t+\tau}'} = \mathcal{J} = 1$

generaliz. za 2 varijable



$$\begin{vmatrix} \frac{\partial Q_1}{\partial z_1} & \cdots & \frac{\partial Q_s}{\partial z_1} & \frac{\partial P_1}{\partial z_1} & \cdots & \frac{\partial P_s}{\partial z_1} \\ \vdots & & & & & \\ \frac{\partial Q_1}{\partial P_s} & \cdots & \frac{\partial Q_s}{\partial P_s} & \frac{\partial P_1}{\partial P_s} & \cdots & \frac{\partial P_s}{\partial P_s} \end{vmatrix} = \begin{vmatrix} \frac{\partial Q_1}{\partial z_1} & \cdots & \frac{\partial Q_s}{\partial z_1} & \frac{\partial P_1}{\partial z_1} & \cdots & \frac{\partial P_s}{\partial z_1} \\ \vdots & & & & & \\ \frac{\partial Q_1}{\partial p_s} & \cdots & \frac{\partial Q_s}{\partial p_s} & \frac{\partial P_1}{\partial p_s} & \cdots & \frac{\partial P_s}{\partial p_s} \end{vmatrix} \cdot \begin{vmatrix} \frac{\partial z_1}{\partial z_1} & \cdots & \frac{\partial z_s}{\partial z_1} & \frac{\partial p_1}{\partial z_1} & \cdots & \frac{\partial p_s}{\partial z_1} \\ \vdots & & & & & \\ \frac{\partial z_1}{\partial P_s} & \cdots & \frac{\partial z_s}{\partial P_s} & \frac{\partial p_1}{\partial P_s} & \cdots & \frac{\partial p_s}{\partial P_s} \end{vmatrix}$$

$$\frac{\partial(Q_1 \dots Q_s, P_1 \dots P_s)}{\partial(z_1, \dots z_s, P_1, \dots P_s)} = \frac{\partial(z_1 \dots z_s, P_1 \dots P_s)}{\partial(z_1, \dots z_s, P_1, \dots P_s)} \cdot \frac{\partial(Q_1, \dots Q_s, P_1, \dots P_s)}{\partial(z_1, \dots z_s, p_1, \dots p_s)} = \Pi$$

$$\begin{vmatrix} \frac{\partial Q_1}{\partial z_1} & \cdots & \frac{\partial Q_s}{\partial z_1} & \frac{\partial P_1}{\partial z_1} & \cdots & \frac{\partial P_s}{\partial z_1} \\ \vdots & & \frac{\partial Q_i}{\partial z_k} & & & \\ \frac{\partial Q_1}{\partial z_s} & \cdots & \frac{\partial Q_s}{\partial z_s} & \frac{\partial P_1}{\partial z_s} & \cdots & \frac{\partial P_s}{\partial z_s} \\ 0 & \cdots & 0 & 1 & \cdots & 0 \\ \vdots & & \vdots & \vdots & \ddots & \vdots \\ 0 & \cdots & 0 & 0 & & 1 \end{vmatrix} = \begin{vmatrix} 1 & \cdots & 0 & 0 & \cdots & 0 \\ 0 & 1 & & \vdots & & \vdots \\ \vdots & & \ddots & 0 & & \vdots \\ 0 & \cdots & 1 & 0 & \cdots & 0 \\ \frac{\partial z_1}{\partial P_1} & \cdots & \frac{\partial z_s}{\partial P_1} & \frac{\partial p_1}{\partial P_1} & \cdots & \frac{\partial p_s}{\partial P_1} \\ \vdots & & \vdots & \frac{\partial p_k}{\partial P_i} & & \\ \frac{\partial z_1}{\partial P_s} & \cdots & \frac{\partial z_s}{\partial P_s} & \frac{\partial p_1}{\partial P_s} & \cdots & \frac{\partial p_s}{\partial P_s} \end{vmatrix} \cdot \Pi$$

$$\Rightarrow \quad \Pi = \frac{\left\{ \frac{\partial(Q_1, \dots Q_s)}{\partial(z_1, \dots z_s)} \right\}_{P=\text{const}}}{\left\{ \frac{\partial(P_1, \dots P_s)}{\partial(P_1, \dots P_s)} \right\}_{z=\text{const}}} \quad \rightarrow \text{smatramo pri tom parc. derivacije}$$

$$Q_i = \frac{\partial \phi}{\partial P_i}$$

Kanonska transf.

(i) $\rightarrow$ $\left(\frac{\partial Q_i}{\partial z_k}\right)_{z_i} = \frac{\partial^2 \phi}{\partial z_k \partial P_i}$ $\qquad$ $p_k = \frac{\partial \phi}{\partial z_k}$ $\qquad$ $\left(\frac{\partial p_k}{\partial P_i}\right)_{z_k} = \frac{\partial^2 \phi}{\partial z_k \partial P_i}$ $\qquad$ & $|A^T| = |A|$

$$\Rightarrow \quad \underline{\Pi = 1} \qquad \text{za Kanonska transf.}$$

$$\Delta\phi' = \int_{\Delta\phi} \cdots \int dz_1 \cdots dp_s$$

$\rightarrow$ $\forall$ točka danog volumena $\Delta\phi'$ ($\overbrace{\text{dijela } \Delta\phi}$) faznog prostora pomiče se s vremenom prema jba. gibanja promatranog fizičkog sistema $\Rightarrow$ time se pomiče dio $\Delta\phi$ kao cjelina $\rightarrow$ $\underline{\Delta\bar{\phi}}$ kopija volumena $\Delta\bar{\phi}'$

i pri tom $\underline{\Delta\phi' = \Delta\bar{\phi}'}$ Liouville-ov.

→ Liouville-tm izlazi iz <u>invarijantnosti</u> faznog volumena pri kanonskim transformacijama, a sama prompena p & q pri kretanju može se smatrati kao kanonska transformacijama

→ Kanon. transf. (3) (26a'') $i=1,\dots s$

$$q_{i_t}, p_{i_t} \to q_{i_{t+\tau}}, p_{i_{t+\tau}} \quad \Rightarrow \quad \Delta\phi_t \to \overline{\Delta\phi}_{t+\tau}$$

$$\Rightarrow \lim_{\Delta\phi_t' \to 0} \frac{\Delta\phi_t'}{\overline{\Delta\phi}_{t+\tau}'} = \mathrm{J} = 1$$

$$\mathrm{J} = \frac{\partial(q_{1_t}, \dots p_{s_t})}{\partial(q_{1_{t+\tau}}, \dots p_{s_{t+\tau}})} = 1$$

$$\Delta\phi_t' = \int_{\Delta\phi_t} \dots \int dq_{1_t} \dots dp_{s_t} = \int_{\overline{\Delta\phi}_{t+\tau}} \dots \int \mathrm{J}\, dq_{1_{t+\tau}} \dots dp_{s_{t+\tau}} = \overline{\Delta\phi}_{t+\tau}'$$

analogno moš. dokazati invarijantnost integrala: (za kanonske transformacije)

$$\iint \sum_i dq_i \cdot dp_i$$

$$\iiii \sum_{i \neq k} dq_i\, dp_i\, dq_k\, dp_k$$

. . . . . .

sistem N čestica $\rightarrow$ $S = s\,N$

$$dW = \frac{1}{N!\,h^S}\cdot\frac{1}{Z}\,e^{-\frac{1}{\theta}H(q_1,\dots p_s,a)}\,d\phi \qquad d\phi = \frac{e^{-\frac{1}{\theta}H(q_1,\dots p_s,a)}}{\int_\Gamma e^{-\frac{1}{\theta}H(q_1,\dots p_s,a)}\,d\phi} \qquad Z = \frac{1}{N!\,h^S}\int_\Gamma e^{-\frac{1}{\theta}H(q_1,\dots p_s,a)}\,d\phi$$

$$dW^{(E)} = \frac{1}{N!\,h^S}\cdot\frac{1}{Z}\,e^{-\frac{E}{\theta}}\,\Omega(E,a)\,dE \qquad Z = \frac{1}{N!\,h^S}\int_{(E)} e^{-\frac{E}{\theta}}\,\Omega(E,a)\,dE$$

3.5. Maxwell - Boltzmann-ova formula

→ 1 molek. u t-dim. uramoteženom plinu T

→ ako **interakcija među molekulama slaba** (ako su intermolek. sile kratkog dometa, tada molek. interagiraju samo u akcu sudara, dakle u dotku vremena koje je zanemarivo malo spram vremena njihovog slobodnog puta)

na papirima:

$$\Rightarrow \mathcal{H}_{int_h} = U_{h\,int.}(q_1,\dots q_S) \approx 0 \quad \text{za } \forall h = 1,\dots N$$

u usporedbi s ostalim članovima u $\mathcal{H}_h$ jednomolek. !! zanemarivo

energija interakcije h-te molek. s termost. $\mathcal{T}\cdot(N-1)$ molek.

$$\Rightarrow H(q_1,\dots p_S,a) = \sum_{h=1}^{N}\left\{T_h^{tot}(q_{h1},\dots q_{hs},\dot q_{h1},\dots \dot q_{hs}) + U_h^{tot}(q_{h1},\dots q_{hs})\right\}$$

$$= \sum_{h=1}^{N} H_h(q_{h1},\dots q_{hs},\dot q_{h1},\dots \dot q_{hs}) \qquad \left(= \sum_{k=1}^{s} q_{hk}\frac{\partial L_h}{\partial \dot q_{hk}} - L_h\right)$$

$$= \sum_{h=1}^{N} H_h(q_{h1},\dots q_{hs},p_{h1},\dots p_{hs}) \qquad \text{gdje } p_{hk} = \frac{\partial L_h}{\partial \dot q_{hk}}$$

$$dW = \frac{e^{-\frac{1}{\theta}H(q_1,\dots p_S,a)}}{\int_\Gamma e^{-\frac{1}{\theta}H(q_1,\dots p_S,a)}\,d\phi} = \prod_{h=1}^{N}\frac{e^{-\frac{1}{\theta}H_h(q_h\dots p_h)}}{\int_{(\mu_h)} e^{-\frac{1}{\theta}H_h(q_h\dots p_h)}\,dq_{h1}\dots dp_{hs}} = \prod_{h=1}^{N} dW_h$$

pogledaj dopunu

$$\Rightarrow dW_h = \frac{\frac{1}{h^s}e^{-\frac{1}{\theta}H_h(q_{h1},\dots p_{hs})}\,dq_{h1}\dots dp_{hs}}{\frac{1}{h^s}\int_{(\mu_H)} e^{-\frac{1}{\theta}H_h(q_{h1},\dots p_{hs})}\,dq_{h1}\dots dp_{hs}}$$

– vjerojatnost da se molekula nalazi u elementu volumena (μ- prostora $q_{h1}, q_{h1}+dq_{h1} \dots p_{hs}, p_{hs}+dp_{hs}$

budući je $dW = \prod_{h=1}^{N} dW_h$ što vrijedi samo za nezav. molekule

$\Rightarrow$ **možemo uočenu molekulu smatrati kao zasebni fizikalni sistem u slaboj interakciji s termostatom, koji predstavljaju ostale molekule**

$$\mathcal{H}_h(q_1,\dots p_S) = H_h = \underbrace{T_h^{tot}(q_{h1},\dots q_{hs},p_{h1},\dots p_{hs}) + U_h^{tot}(q_{h1},\dots q_{hs})}_{\mathcal{H}_{0_h}(q_{h1},\dots p_{hs})} + \underbrace{U_{h\,int.}(q_1,\dots q_S,\blacksquare\blacksquare\blacksquare p_S)}_{\mathcal{H}_{int_h}(q_1,\dots q_S)}$$

$\mathcal{H}_{0_h}(q_{h1},\dots p_{hs})$ – obuhvaća vlastitu energiju molekule (kin. energiju centra mase, potencijalnu energiju centra mase uslijed vanj. sila, kin. & pot. energiju uslijed rotacionog i oscilacionog gibanja oko centra mase)

Kraće $\mathcal{H}_0(q_1,\dots q_s,p_1,\dots p_s)$

$S = s \cdot N$

$\mathcal{H}_{int}(q_1, \dots q_S, p_1, \dots p_S)$ - energija interakcije molek. s termostatom, $\mathcal{H}$: s ostalih $(N-1)$ molekula

$$\mathcal{H}_h(q_1, \dots p_S) = \mathcal{H}_{o_h}(q_1, \dots p_S) + \mathcal{H}_{int_h}(q_1, \dots q_S)$$

V_h - volumen h-te molek.

$$U_{h_{int}}(q_1, \dots p_S) = \int_{V_h} \sum_{h \neq j=1}^{N} U_j(x-x_j, y-y_j, z-z_j, \varphi_j, \vartheta_j, \psi_j)\, dV$$

$$= \sum_{h \neq j=1}^{N} \int_{V_h} U_j(x-x_j, y-y_j, z-z_j, \varphi_j, \vartheta_j, \psi_j)\, dV$$

(Koordinata) opcenito svih kan. varijabli jer pot. energija ovisi i o trenutnom položaju atoma pri oscilacijama

$\Rightarrow$ **originalno!!**

$$\mathcal{H}_{int_h}(q_1, \dots q_S) = \sum_{h \neq j=1}^{N} \mathcal{U}^{*}_{gj_{int}}(q_{h_1}, \dots q_{h_S}, q_{j_1}, \dots q_{j_S})$$

$$U_{gj_h}(x_h, y_h, z_h, \varphi_h, \vartheta_h, \psi_h, x_j, y_j, z_j, \varphi_j, \vartheta_j, \psi_j)$$

$x_{h_1}, \dots x_{h_{S_{os.}}}$; $x_{j_1}, \dots x_{j_{S_{os.}}}$ — parcijalni int

j-ta na h-tu

$\vec{F}_{jh} = -\text{grad}_h U_{jh}$

$U_{gj_{int}}$ - predstavlja energiju interakcije h-te molek. samo sa j-tom molekulom

očito $\mathcal{H}_{int_h} \gg U_{gj_{int}}$ **i)** $\forall j = 1, \dots N \neq h$

$\Rightarrow$ zbog toga možemo smatrati da se h-ta & j-ta molek. praktički nezavisno jedna s pram druge, a to naime slijedi iz činjenice da zahtjevamo već da $\forall$ molekula slabo interagira (ali ipak interagira) s termostatom $\mathcal{H}$. s preostalih $(N-1)$ molek. sistema $\mathcal{H}$. $\mathcal{H}_{int_h}$ malen **ii)** pa je dodatak $U_{gj_{int}}$ zanemariv

$\Rightarrow$ h-ta & K-ta molek. možemo smatrati gotovo nezav. sistema, pa je vjerojatnost realizacije ukupnog stanja = produkt vjerojatnosti realizacije parcijalnih stanja

$$dW_{K,h} = dW_h \cdot dW_K \quad (1)$$

parcijalni

$$\mathcal{H}_{K,h} = \mathcal{H}_h(q_1, \dots p_S) + \mathcal{H}_K(q_1, \dots p_S) = \mathcal{H}_{oh}(q_{h_1}, \dots p_{h_S}) + \mathcal{H}_{oK}(q_{K1}, \dots p_{K_S}) + \mathcal{H}_K$$

$$+ \sum_{K, h \neq j=1}^{N} U^{*}_{gj_{int}}(q_{h_1}, \dots q_{h_S}, q_{j_1}, \dots q_{j_S}) + \sum_{h, K \neq j=1}^{N} U^{*}_{gj_{K,int}}(q_{K1}, \dots q_{K_S}, q_{j_1}, \dots q_{j_S})$$

$\mathcal{H}_h \approx$

interakcija h-te molek. s termostatom i $(N-2)$ molek.

$$+ \underbrace{U^{*}_{K,h_{int}}(q_{h_1}, \dots q_{h_S}, q_{K1}, \dots q_{K_S}) + U^{*}_{h,K_{int}}(q_{K_1}, \dots q_{K_S}, q_{h_1}, \dots q_{h_S})}_{\mathcal{H}_{K,h_{int}} \approx 0 \quad \text{zbog i) \& ii)}}$$

$\Rightarrow$ (2) $\mathcal{H}_{K,h} \cong \mathcal{H}_h + \mathcal{H}_K$ gdje $\mathcal{H}_h$ ne ovisi o varijablama K-te molek.

dopuna (26) c) I strana

$$dW = \frac{e^{-\frac{1}{\Theta}H(q_1,\dots p_s,a)}}{\int_\Gamma e^{-\frac{1}{\Theta}H(q_1,\dots p_s,a)}}$$

$$H(q_1,\dots p_s,a) = \overset{T+U}{\sum_{h=1}^{N}}\left[\frac{1}{2}m_h S\dot{x}_h^2 + SS' a_{\varphi_h\varphi_h}(\varphi_h,\psi_h,\vartheta_h)\dot{\varphi}_h\dot{\psi}_h + \right.$$

$$\left. + \sum_{k=1}^{s_{os.}}\frac{1}{2}m_{hk}\dot{x}_{hk}^2\right] +$$

$$+\sum_{h=1}^{N}\left\{U_{vh}\underbrace{(x_h,y_h,z_h,\varphi_h,\psi_h,\vartheta_h)}_{\text{koord. centra mase}\ (\text{ne ovisi o oscilacijama vlastitim})} + \sum_{k=1}^{s_{os.}}\frac{4\pi^2 m_{hk}\nu_{hk}^2 x_{hk}^2}{2} + \right.$$

$$\left. + \sum_{h\neq j=1}^{N} U^{*}_{jh_{int.}}\underbrace{(z_{h1},\dots z_{hs},z_{j1},\dots z_{js})}_{(x_h,y_h,z_h,\varphi_h,\psi_h,\vartheta_h,x_j,y_j,z_j,\varphi_j,\psi_j,\vartheta_j)\ \to \text{na (*****)}}\right\} \quad \text{ili } \sum_{j=1}^{N}\ \text{za } U_{hh}=0$$

$$\underbrace{f_{int_h}(z_1,\dots z_s)}_{(x_h,y_h,z_h,z_1,\dots z_{3(N-1)})} \qquad s=s\cdot N$$

→ako divergiju molekule (sobzirom na ROT. & OSC.) nemaju utjecaja na interakciju izmedju dvije molekule (budući su dedim. molekule tako da je dužina njih promjena potenc. energije od drugih (N-1) molek. neznatna), dada možemo smatrati da imamo interakciju između materijalnih točaka dviju njihovih spojnica

$$\vec{r}_{jh} = \vec{r}_h - \vec{r}_j$$

$$\Rightarrow \underbrace{f_{int_h}(z_1,\dots z_s)}_{\text{bez } *} = \frac{1}{2}\sum_{j=1}^{N} U_{jh}(x_h-x_j, y_h-y_j, z_h-z_j) \qquad U_{hh}\equiv 0$$

*) iz (26.a)

h-ta molek.

x_h, y_h, z_h (3), $\varphi_h, \psi_h, \vartheta_h$ (3), $x_{h1}, \dots x_{hk}, \dots x_{hs_{os.}}$ ($s_{os.}$)

st. slobode $s_{os.} + 6 = s$ za 1 molek.

q_{h1} ↕ $q_{hs-(s-1)}$; q_{hs} ↕ $q_{h\cdot s}$

$S = N \cdot s$

$$L(q_1, \dots q_s) = T - U$$

$$= \sum_{i=1}^{s}\sum_{j=1}^{s} Q_{ij}(q_1, \dots q_s)\dot{q}_i \dot{q}_j - U(q_1, \dots q_s)$$

$$p_k = \frac{\partial L}{\partial \dot{q}_k} \qquad \sum_{h=1}^{N} L_h = L = \sum_{h=1}^{N} \{ T_h^{tot.}(q_{h1}, \dots \dot{q}_{hs}, \dot{q}_{h1}, \dots q_{hs}) -$$

$$\Rightarrow p_{hk} = \frac{\partial L_h}{\partial \dot{q}_{hk}} \quad \text{Lag. energija tot. h-te molek.} \qquad - [U_h^{tot.}(q_{h1}, \dots q_{hs}) + U_{h_{int.}}(q_1, \dots q_s)] \}$$

$$\Rightarrow \underbrace{p_{hk} = \frac{\partial L}{\partial \dot{q}_{hk}}}_{k=1,\dots s} = f_{hk}(q_{h1}, \dots q_{hs}, \dot{q}_{h1}, \dots \dot{q}_{hs}) \quad \text{nelinearna}$$

p_{hk} gen. impuls h-te molekule na ovisi o gen. koord. ostalih molekula

za klas. meh. & klas. sile:

ranj. utjecaj polja → na pod. ansamb. molek.

$$H(q_1 \dots p_s, t) = T + U$$

$$= \sum_{h=1}^{N} \left\{ T_h^{tot}(q_{h1}, \dots q_{hs}, \dot{q}_{h1} \dots \dot{q}_{hs}) + \right.$$

$$+ U_h^{tot}(q_{h1}, \dots q_{hs}) +$$

$$\left. U_{h\,int.}(q_1 \dots q_g) \right\}$$

(30K) iz (26.0)

1 molekula - u sustavu težišta (centra mase)

opća elastična sila (↑ atom titra oko srog položaja ramoteže u molekuli)

$$\vec{F}(\vec{r}) = \vec{F}(x,y,z) = \sum_{i,j,k=0}^{\infty} \vec{a}_{ijk}\, x^i y^j z^k$$

zahtjev $\vec{F}(0) = 0 \Rightarrow \vec{a}_{000} = 0$

(težište ↑ atoma izvodi zbog prisustva drugih atoma - veze s njima oscilacije oko srog položaja ramoteže i to općenito u svakoj smjeru u prostoru)

za male pomake: (zanemarivi viši članovi - potencije i produkti)

$$\vec{a}_{100} = -k_1^2 \vec{i} \qquad \vec{a}_{010} = -k_2^2 \vec{j} \qquad \vec{a}_{001} = -k_3^2 \vec{k}$$

$$\Rightarrow \vec{F}(\vec{r}) \approx -k_1^2 \cdot x\, \vec{i} - k_2^2 \cdot y\, \vec{j} - k_3^2 \cdot z \cdot \vec{k}$$ harmonička sila

ako ima n-atoma u molek. $\Rightarrow 3 \cdot n = s_{osc.}$ general. koord. po kojima se vrše oscilacije

$\Rightarrow$ general. sila - elastična za h-tu molek.

$$\vec{F}_{hosc} \equiv \left(-k_{h_1}^2 \cdot Q_{h_1} q_1 \cdots , -k_{h_{s_{osc.}}}^2 \cdot Q_{h s_{osc.}} \right)$$

N - molekula $\quad Q_{h_1} \equiv X_{(h \cdot s_{osc.} - (s_{osc.} - 1))} \quad \cdots \quad Q_{h_{s_{osc.}}} \equiv X_{(h \cdot s_{osc.})}$

(a 25 str (xx)

→ generaliz. elast. sila za N-molekula

$N \cdot s_{osc.}$ - gen. koord. oscilacija

$$\vec{F}_{c_{osc}} \equiv (\vec{F}_{1_{osc}}, \dots, \vec{F}_{n_{osc}}, \dots \vec{F}_{N_{osc.}})$$

$$\equiv (X_1^{os.}, \dots X_i^{os.}, \dots X_{N\cdot s_{osc.}}^{os.})$$

$$\equiv \left(-k_1^2 \cdot x_1, \dots -k_i^2 x_i, \dots, -k_{N\cdot s_{osc.}}^2 \cdot x_{N\cdot s_{osc.}}\right)$$

$$d'R_{osc.} = \vec{F}_{c_{osc}} \cdot d\vec{r}_{c_{osc}} \qquad \text{gdje } \vec{r}_{c_{osc.}} \equiv (x_1^{osc.}, \dots x_i^{os.}, \dots x_{N\cdot s_{osc.}}^{os})$$

$$d\vec{r}_{c_{osc}} \equiv (dx_1^{osc}, \dots, dx_{N\cdot s_{osc}}^{os.})$$

$$= \sum_{i=1}^{(N\cdot s_{osc.})} X_i \cdot dx_i^{os.} = -dU^{os.}$$

$$X_i^{os.} = -\frac{\partial}{\partial x_i}\left(\frac{k_i^2 x_i^{os\,2}}{2}\right) = -\frac{\partial U_i^{os.}}{\partial x_i} \qquad U_i^{os.} = \frac{1}{2} k_i^2 x_i^{os\,2}$$

$$U^{osc.}(x_1^{os.}, \dots x_{N\cdot s_{os.}}^{os.}) = \frac{1}{2}\sum_{i=1}^{(N\cdot s_{os.})} k_i^2 x_i^{os\,2} \Rightarrow \vec{F}_{c_{osc.}} = -\text{grad}_{c_{osc.}} U^{osc.}$$

$$= \sum_{i=1}^{N\cdot s} U_i^{osc.}$$

za takve harmon. oscilacije:

$$m\ddot{x} + k^2 x = 0$$

$$\ddot{x} + \frac{k^2}{m} x = 0$$

$$\omega^2$$

$$k_i^2 = m_i \cdot \omega_i^2 = \frac{4\pi^2 m_i}{T_i^2} = 4\pi^2 m_i \nu_i$$

(1 / atom umolek. mjesta mase)

$$\Rightarrow U_i^{osc.} = \frac{4\pi^2 m_i \nu_i \cdot x_i^{os\,2}}{2}$$

(molek) u2 (6 0)

Promatrajmo gibanje 1 molek. kao gibanje krutog tijela
→ sustav slob. os. postavimo u težište (centar mase) molek.
⇒ sustav glavnih os.

$$\Rightarrow 2T = m V_T^2 + \sum_{i=1}^{3} I_i \cdot \omega_i^2$$

$T = \frac{1}{2} \int_V \vec{v} \cdot dm$

$U_V = \int_V dU_V = \lim_{n\to\infty} \sum_{h=1}^{n} \Delta U_h$

Kin. energija h-te molekule:

$$T_h = \frac{1}{2} S m_h \dot{x}_h^2 + \frac{1}{2} S I_{\xi h} \omega_{\xi h}^2$$

x_h, y_h, z_h Kartez. koord. centra mase molekule

$\frac{1}{2} S' I_{\xi h} \omega_{\xi h}^2 = S S' a_{\varphi\psi}(\varphi_h, \psi_h, \vartheta_h) \cdot \dot{\varphi}_h \dot{\psi}_h$

i) $\omega_{\xi h}(t) = \sin\psi_h \sin\vartheta_h \dot{\varphi}_h + \cos\psi_h \dot{\vartheta}_h$

ii) $\omega_{\eta h}(t) = \cos\psi_h \sin\vartheta_h \dot{\varphi}_h - \sin\psi_h \dot{\vartheta}_h$

iii) $\omega_{\zeta h}(t) = \dot{\psi}_h + \cos\vartheta_h \dot{\varphi}_h$

Kin. energija cijelog sistema od N molekula:

$$T = \sum_{h=1}^{N} T_h = \sum_{i=1}^{6N} a_i \cdot \dot{x}_i^2$$

$a_{6h-5} = \frac{1}{2} m_h$ . . . . $a_{6h} = \frac{1}{2} I_{\zeta h}$

$\dot{x}_{6h-5}^2 = \dot{x}_h^2$ $\dot{x}_{6h}^2 = \omega_{\zeta h}^2$

$x_{6h-5} = x_h = q_{6h-5}$ $x_{6h-4} = y_h = q_{6h-4}$ $x_{6h-3} = z_h = q_{6h-3}$

$x_{6h-2} = x_{6h-2}(q_{6h-2}, q_{6h-1}, q_{6h})$ $q_{6h-2} = \varphi_h$

$x_{6h-1} = x_{6h-1}(q_{6h-2}, q_{6h-1}, q_{6h})$ $q_{6h-1} = \psi_h$

$x_{6h} = x_{6h}(q_{6h-2}, q_{6h-1}, q_{6h})$ $q_{6h} = \vartheta_h$

$$\Rightarrow T = \sum_{i=1}^{6N} \sum_{j=1}^{6N} Q_{ij}(q_1 \dots q_{6N})\, \dot{q}_i \dot{q}_j$$

$$T = \sum_{h=1}^{N} \left[\tfrac{1}{2} m_h S \dot{x}_h^2 + SS' a_{\varphi_h \psi_h}(\varphi_h, \psi_h, \vartheta_h) \cdot \dot{\varphi}_h \dot{\psi}_h \right]$$

gdje: x_h, y_h, z_h Kartez. koord. centra mase (tez. sth.) molekule

$\varphi_h, \psi_h, \vartheta_h$ Eulerovi kutevi sustava slob. osi (u tez. sth.) spram kartez. pravok. sustava

\+ (rotacija)

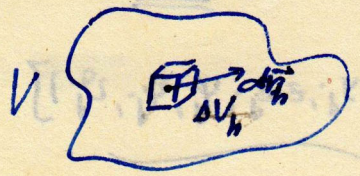
Ukupna kin. energija sistema od N-molek.

$$T = \sum_{h=1}^{N} \left[\underbrace{\tfrac{1}{2} m_h S \dot{x}_h^2}_{\text{3-gen. koord.}} + \underbrace{SS' a_{\varphi_h \psi_h}(\varphi_h, \psi_h, \vartheta_h) \cdot \dot{\varphi}_h \dot{\psi}_h}_{\text{3-gen. koord.}} + \underbrace{\sum_{k=1}^{3n-6} \tfrac{1}{2} m_{hk} \dot{x}_{hk}^2}_{\text{harm. oscilacije unutar } h\text{-te molekule}} \right]$$

(lin. q.b. centra mase molek.; rotacija molek.; $3n-6$ osc.-gen. koord.)

$$T = \sum_{h=1}^{N} \left[\underbrace{T_h + T_{h\,rot}}_{T_h^{tot.}} + T_{h\,osc.} \right]$$

(*****) $\vec{F} = \varrho \vec{E} = V \varrho_z \vec{E} =$



$\vec{F} = -\text{grad}\, U(x,y,z)$

$d\vec{F} = -\text{grad}\,(dV \cdot \mu(x,y,z)) = dV \cdot [-\text{grad}\, u(x,y,z)]$

$= dV \cdot \vec{I}$

↑ tijela

podijelimo tijelo V na n dijelova

$$V = \sum_{h=1}^{n} \Delta V_h$$

→ u središtu ΔV_h uzmemo vrijednost sile i to dobivenu usrednjavanjem po tom malom volumenu, bolje rečeno: zbog teorije $U(x,y,z)$ neka vrijednost, dijeli u neku pogodnu točku ΔV_h

neka $(\xi_h, \eta_h, \zeta_h) \in \Delta V_h$

$$\vec{F}_h = -\text{grad}\, U(\xi,\eta,\zeta) = -\text{grad}_h \left[\Delta V_h^{(\xi_h,\eta_h,\zeta_h)} \cdot \mu(\xi_h,\eta_h,\zeta_h)\right]$$

↑ tijela

$$= \Delta V_h \cdot [-\text{grad}_h\, \mu(\xi_h,\eta_h,\zeta_h)]$$

↖ uzeto u toj odabranoj točki

$$d'R = \sum_{h=1}^{n} \vec{F}_h \cdot d\vec{r}_h = -\sum_{h=1}^{n} \Delta V_h\, \text{grad}_h\, \mu(\xi_h,\eta_h,\zeta_h) \cdot d\vec{r}_h$$

$$= -\sum_{h=1}^{n} \Delta V_h \cdot d\mu_h(\xi_h,\eta_h,\zeta_h) = -d \sum_{h=1}^{n} \Delta V_h \cdot \mu_h(\xi_h,\eta_h,\zeta_h)$$

↑ tj. parc. diferr. dog tj. uzeto u toj točki

$$d'R = -d\left\{\lim_{n\to\infty} \sum_{h=1}^{n} \Delta V_h \cdot \mu_h(\xi_h,\eta_h,\zeta_h)\right\} = -d \int_V \mu(x,y,z)\, dV$$

$$= -d \int_V dU(x,y,z) = -d\, U(x_T, y_T, z_T, \psi, \psi, \vartheta)$$

↑ fizičko mjerilo

(?) jer K ovisi pod. energ. razj. malim o 2or.

(*****)

→ vanjske pole sile, ali kot poteče od ostalih $N-1$ molekul a dejstvuje na h-ti molek.

$$\vec{F}_{int.} = \sum_{h\neq j=1}^{N} \vec{F}_{jh} = -\operatorname{grad}\Big[\underbrace{\sum_{h\neq j=1}^{N} U_{jh}(x-x_j, y-y_j, z-z_j, \varphi_j, \psi_j, \vartheta_j)}_{U(x,y,z,\, x_j, y_j, z_j, \varphi_j, \psi_j, \vartheta_j)\quad j=1,\dots N \neq h}\Big]$$

poh-bj molekul: $\Delta \vec{F}_{int_h} = \Delta V \cdot \{-\operatorname{grad} \underbrace{u(x,y,z, x_j, y_j, z_j, \varphi_j, \psi_j, \vartheta_j)}_{\sum_{h\neq j=1}^{N} u_{jh}}\}$

analogno:

$$d'R_{\substack{\eta \\ molek.}} = -d\Big(\underbrace{\int_{V_h} u(x,y,z, x_j, y_j, z_j, \varphi_j, \psi_j, \vartheta_j)\, dV_{(x,y,z)}}_{U_{h_{int.}}}\Big) \quad h\neq j=1,\dots N$$

po volum. h-te molek.

⇒ potenc. energija interakcije h-te molekule

$$U_{h_{int}}(x_i, y_i, z_i, \varphi_i, \psi_i, \vartheta_i) = \int_{V_h} u(x,y,z, x_j, y_j, z_j, \varphi_j, \psi_j, \vartheta_j)\, dV$$

$i = 1,\dots N \qquad h\neq j = 1,\dots N$

→

$d'R = d'R_v + d'R_{in}$

$$d'R_{in} = \sum_{h=1}^{N} \int_{V_h} \sum_{h\neq j=1}^{N} d\vec{F}_{jh} \cdot d\vec{r}_h$$

$$= \sum_{h=1}^{N} \Big(\int_{V_h} -\sum_{h\neq j=1}^{N} \operatorname{grad}_h U_{jh}(x_h, y_h, z_h, x_j, y_j, z_j, \varphi_j, \psi_j, \vartheta_j)\, dV_h \cdot d\vec{r}_h \Big)$$

$$= -\sum_{h=1}^{N} \sum_{h\neq j=1}^{N} \int_{V_h} \operatorname{grad}_h u_{jh}(x_h, y_h, z_h, x_j, y_j, z_j, \varphi_j, \psi_j, \vartheta_j)\, d\vec{r}_h \cdot dV_h$$

$dx_h dy_h dz_h$

$$d'U_{jh}^{int}(x_h, y_h, z_h, \varphi_h, \psi_h, \vartheta_h, x_j, y_j, z_j, \varphi_j, \psi_j, \vartheta_j)$$

$d\vec{F}_{jh} = -\operatorname{grad}_h U_{jh}(x_h, y_h, z_h, x_j, y_j, z_j, \varphi_j, \psi_j, \vartheta_j) \cdot dV_h$ — potencijal (ne potenc. energija)

$U_{jh} \equiv 0$

(*****) iz (26) c)

nastavak (***)

→ u molekuli n-atoma (skupina) koji mogu titrati · opć.
u 3 smjera prostora općenito

$S_{os.}$ – ukupni broj (stupnjeva slob.) mogućih oscilacija u molekuli

vrijedi $S_{osc.} \approx 3 \cdot n$

– toliko gen. koord. za oscilacije u h molekuli:

$$x_{h1}, \ldots x_{hk}, \ldots x_{hS_{osc.}}$$

x_{hk} – udalj. od položaja ravnoteže k-tog dijela koji titra u h-toj molekuli

Kin. energ. oscilacija h-te molekule:

$$T_h^{osc.} = \sum_{k=1}^{S_{osc.}} \frac{1}{2} m_{hk} \dot{x}_{hk}^2 \qquad (*****)$$

$$\Rightarrow T^{osc.} = \sum_{h=1}^{N} \left(\sum_{k=1}^{S_{osc.}} \frac{1}{2} m_{hk} \dot{x}_{hk}^2 \right)$$

ukupna pot. energija h-te molek.:

$$U_h^{osc.} = \sum_{k=1}^{S_{osc.}} \frac{4\pi^2 \nu_{hk}^2 x_{hk}^2}{2}$$

$$U^{osc.} = \sum_{h=1}^{N} \left(\sum_{k=1}^{S_{osc.}} \frac{4\pi^2 \nu_{hk}^2 x_{hk}^2}{2} \right)$$

U_u = const. za kruto tijelo

$U_V = \int_V dU_V = \lim_{n\to\infty} \sum_{h=1}^{n} \Delta U_{Vh}$ pot. energija krutog dijela zbog vanj. polja sila

$d\vec{F} = \vec{f}\, dV \quad \vec{f} = -\text{grad}\, u(x,y,z)$

ukupna pot. energ. h-te molek. $U_{Vh} = \int_{V_h} dU_V = U_{Vh}(x_h, y_h, z_h, \varphi_h, \psi_h, \vartheta_h)$ gdje $\vec{F} = -\text{grad}\, U(x,y,z)$

u vanjskom polju sile $\vec{F}$ $dU_V = u(x,y,z)\,dV$ a nevise $\vec{F}_h = -\text{grad}_h U_h(\vec{r}_h)$

$$\vec{F}_j = -\text{grad} U_j (x - x_j, y - y_j, z - z_j, \varphi_j, \psi_j, \vartheta_j)$$

polje sile koje potječe od j-te molekule

gdje: $x_j, y_j, z_j, \varphi_j, \psi_j, \vartheta_j$ koord. koje određuju položaj j-te molekule

ukupno polje sila koje djeluje na h-tu molekulu

$$\sum_{h\neq j=1}^{N} \vec{F}_j = -\text{grad} \left[\sum_{h\neq j=1}^{N} U_j (x - x_j, y - y_j, z - z_j, \varphi_j, \psi_j, \vartheta_j) \right]$$

$$R_h = \int_{V_h} \left(\sum_{h\neq j=1}^{N} \vec{F}_j \right) d\vec{r} = -\int_{V_h} d \left[\sum_{h\neq j=1}^{N} U_j (x - x_j, y - y_j, z - z_j, \varphi_j, \psi_j, \vartheta_j) \right]$$

pogledaj na

Ukupna potenc. energija sistema od N-molekula

$$U = \sum_{h=1}^{N} \left\{ U_{Vh}(x_h, y_h, z_h, \varphi_h, \psi_h, \vartheta_h) + \sum_{k=1}^{3n} \frac{4\pi^2 m_{hk} \nu_{hk}^2 x_{hk}^2}{2} + \right.$$

pot. energija h-te molek. od vanjskog polja sile

ukupna pot. energija h-te molek. od harmon. oscilacija

$$\left. + U_{h_{int}}(x_i, y_i, z_i, \varphi_i, \psi_i, \vartheta_i) \right\}$$

$i = 1, \ldots N$ Ovo!!!

$$U = \sum_{h=1}^{N} \left\{ \underbrace{U_{h_V} + U_{h_{osc.}}}_{U_h^{int}} + U_{h_{int}} \right\}$$

(26) d)

$dW = w \cdot d\phi$

$w = \varphi(H)$

→ sistem u t-dm. ravnoteži (jer i sama molek. kao sistem) ⇒ ergodski sistem

& (1), (2)

⇒ Kanonska raspodjela za molek. kao sistem:

$$dW = A e^{-\frac{1}{\Theta} \mathcal{H}(q_1, \dots p_s, b)} \, dq_1 \dots dp_s$$

$$A = \frac{1}{h^s} \cdot \frac{1}{Z}$$

$$dW = \frac{1}{h^s} \cdot \frac{1}{Z} e^{-\frac{1}{\Theta} \mathcal{H}(q_1, \dots p_s, b)} \, dq_1 \dots dp_s$$

gdje b - označava preostale varijable (molekula) a potječe od stare interakcije s termostatom

$\mathcal{H}$ - s preostalih $(N-1)$ molek. sistema za h-tu molekulu

$$\mathcal{H}_h(q_1, \dots p_s, b) = \mathcal{H}_{oh}(q_1, \dots p_s) + \underbrace{\sum_{h \neq j=1}^{N} U_{jint}(q_{h_1}, \dots q_{hs}, q_{j_1}, \dots q_{j_s})}_{\mathcal{H}_{int\,h}(q_1, \dots q_s)}$$

$$Z = \frac{1}{h^s} \int_{(u)} e^{-\frac{\mathcal{H}(q_1, \dots p_s)}{\chi T}} \, dq_1 \dots dp_s$$

$$Z = \frac{1}{h^s} \int_{(\varepsilon)} e^{-\frac{\varepsilon}{\chi T}} \omega(\varepsilon) d\varepsilon = \int_{(\varepsilon)} e^{-\frac{\varepsilon}{\chi T}} g(\varepsilon) d\varepsilon$$

$\mathcal{H}(q_1, \dots p_s) = \varepsilon$ energija uočene molekule

ima istu vrijednost za različite slogove $(q_1, \dots p_s)$!!

$\omega(\varepsilon)$ - veličina energ. hiperparcine de molekule

$g(\varepsilon) = \frac{\omega(\varepsilon)}{h^s} \cdot d\varepsilon$ - ukupan broj stanja sa podnaškom energijom ε

Koja se mogu međusobno razlikovati

- statistička težina stanja sa energijom ε
- multiplicitet degeneracije energetskog nivoa sa energijom ε

(u kvantnoj meh.)

$$W(q_1, \dots p_s, b) = \frac{1}{h^s} \cdot \frac{1}{Z} e^{-\frac{1}{\chi T} \mathcal{H}(q_1, \dots p_s, b)}$$

- gustoća vjerojatnosti (**) za slog $(q_1 \dots p_s)$

$$W(\varepsilon) = \frac{1}{h^s} \cdot \frac{1}{Z} e^{-\frac{\varepsilon}{\chi T}} \omega(\varepsilon) = \frac{1}{Z} e^{-\frac{\varepsilon}{\chi T}} g(\varepsilon)$$

- gustoća vjer. da mol. ima ukupnu energiju ε (*)

→ vjerojatnost da se uočena molekula nađe u elem. volumenu

$dq_1 \dots dq_s, dp_1 \dots dp_s$ tj. između $q_1, q_1+dq_1 \dots p_s, p_s+dp_s$

$b = \{q_1 \dots q_s$ zbog stalne vel. sa termostatom $(N-1)\}$

$$dW = \frac{e^{-\frac{h(q_1 \dots p_s, b)}{kT}} dq_1 \dots dp_s}{\int_{(\mu)} e^{-\frac{h(q_1 \dots p_s)}{kT}} dq_1 \dots dp_s}$$

Maxwell-Boltzmann-ova formula

→ vjerojatnost da uočena molekula ima energiju između

$\varepsilon, \varepsilon+d\varepsilon$

$$dW^{(\varepsilon)} = \frac{g(\varepsilon) e^{-\frac{\varepsilon}{kT}} d\varepsilon}{\int_{(\varepsilon)} g(\varepsilon) e^{-\frac{\varepsilon}{kT}} d\varepsilon}$$

bitno!! h - te molek.

$$h_h(q_{h1} \dots p_{hs}, b) = h_{0h}(q_{h1} \dots p_{hs}) + h_{int\,h}(q_1 \dots q_s) \qquad S = s \cdot N$$

$$h_{0h} = T_h^{tot}(q_{h1} \dots q_{hs}, p_{h1} \dots p_{hs}) + U_h^{tot}(q_{h1} \dots q_{hs})$$

$$h_{int\,h} = \sum_{h \neq j=1}^{N} U_{j\,int}(q_{h1} \dots q_{hs}, q_{j1} \dots q_{js}) = \sum_{h \neq j=1}^{N} \int_{V_h} u_j(x-x_j, y-y_j, z-z_j, \varphi_j, \psi_j, \vartheta_j)\, dV$$

potencijal koji potječe od j-te molek.

$\vec{f}_j = -\text{grad}\, u_j$ potencijalna sila koja potječe od j-te molek.

****)**

→ Kanonska raspodjela za molekule u μ-prostoru vrijedi i u tom općenitom slučaju gdje je međudjelovanje (energ. interakcija) među molekulama (termostatom), ali

(ii) pod uvjetom da ta interakcija nije toliko jaka da bi pojedinačna energija interakcije ($h_{j,h_{int}} \approx 0$) s nekom K-tom molekulom $U_{K\,int}(q_{h1} \dots q_{hs}, q_{k1} \dots q_{ks})$ imala značajan iznos, dok se za $h_{int\,h} = \sum_{h \neq j=1}^{N} h_{j\,int}$ to dopušta. (v. orig. na (26) c)

→ u protivnom nebi molekule bile nezav. sistemi jedna s pram druge, tj. ne bi mogli koristiti pretp. pri izvod. tzv. raspodjele za vjerojatnost & ukupni hamiltonijan

⇒ iz dih pretp. izlazi Bolt.-Maxw. formula

3.5.5. Zakon ekviparticije – Boltzmann – jednolike raspodjele

$S = s \cdot N$ $\quad$ $s = 6 + S_{os.}$ $\quad$ $\frac{1}{2m_h} S' p_{x_h}^2$

$$\mathcal{H}_h(q_1, \dots p_s) = \frac{1}{2} m_h S \dot{x}_h^2 + S S' a_{\varphi_h \psi_h}(\varphi_h, \psi_h, \vartheta_h) \dot{\varphi}_h \dot{\psi}_h + \sum_{\kappa=1}^{S_{os.}} \frac{1}{2} m_{h\kappa} \dot{x}_{h\kappa}^2 +$$

$$+ \sum_{\kappa=1}^{S_{os.}} \frac{4\pi^2 m_{h\kappa} \nu_{h\kappa}^2 x_{h\kappa}^2}{2} + U_h(x_h, y_h, z_h, \varphi_h, \psi_h, \vartheta_h) +$$

harmonijske oscilacije uočenog atoma u molek. oko njegovog ravnot. položaja. $\quad$ $x_{h_1} \dots x_{hs_{os}}$ $\quad$ $\int_{V_h} \mu(x,y,z)\,dV$

$$+ U_{h_{int}}(x_i, y_i, z_i, \varphi_i, \psi_i, \vartheta_i) = \sum_{h \neq j=1}^{N} \int_{V_h} \mu_j(x - x_j, y - y_j, z - z_j, \varphi_j, \psi_j, \vartheta_j, x_{j_1}, \dots x_{j s_{os}})\,dV$$

$\mathcal{H}_{h_{int.}}$ $\quad$ $i = 1, \dots N$ $\quad$ $U^*_{\mathcal{H}_{h_{int.}}}$

$$\mathcal{H}(q_1 \dots q_s, p_1 \dots p_s, b) = \sum_{\kappa=1}^{l} a_\kappa q_\kappa^2 + \sum_{\kappa=1}^{m} b_\kappa p_\kappa^2 + \mathcal{H}'(q_{l+1} \dots q_s, p_{m+1}, \dots p_s, b)$$

označena skupa ostalih gen. koord. (N−1) molek. $\quad$ Koordinate (N−1) molek.

$l = S_{os.}$ $\quad$ $m = 3 + S_{os.} + 1$ ako imamo rotaciju oko 1 osi: $\quad$ odabrana takva numeracija general. koord. i impulsa da prvih l, m one koje nas interesiraju

→ $(l+m)$ gen. koord. i impulsa (μ-prostora dana kvadratno članova u hamiltonijanu i zovemo ih **energetski stupnjevi slobode**

→ ∀ tip unutarnjih oscilacija molekule (uočenog atoma oko njegovog ravnot. položaja) ima dva energ. stupnja slobode (kin. i pot. energije)

→ ako za promatrane molekule vrijedi ***) , onda i Maxwell-Boltzmann-ova formula

$$\Rightarrow \quad dW = \frac{e^{-\frac{1}{kT}\left[\sum_{\kappa=1}^{l} a_\kappa q_\kappa^2 + \sum_{\kappa=1}^{m} b_\kappa p_\kappa^2 + \mathcal{H}'(q_{l+1}, \dots q_s, p_{m+1}, \dots p_s)\right]} \cdot \prod_{\kappa=1}^{l} dq_\kappa \cdot \prod_{\kappa=1}^{m} dp_\kappa \cdot dq_{l+1} \dots dq_s\, dp_{m+1} \dots dp_s}{\int_{\mu} e^{-\frac{1}{kT}\left[\sum_{\kappa=1}^{l} a_\kappa q_\kappa^2 + \sum_{\kappa=1}^{m} b_\kappa p_\kappa^2 + \mathcal{H}'(q_{l+1}, \dots q_s, p_{m+1}, \dots p_s)\right]} \prod_{\kappa=1}^{l} dq_\kappa \cdot \prod_{\kappa=1}^{m} dp_\kappa \cdot dq_{l+1} \dots dq_s}$$

: zanemarujemo (

$$dW = \prod_{k=1}^{l} \frac{e^{-\frac{a_k q_k^2}{xT}} dq_k}{\int_{-\infty}^{\infty} e^{-\frac{a_k q_k^2}{xT}} dq_k} \cdot \prod_{k=1}^{m} \frac{e^{-\frac{b_k p_k^2}{xT}} dp_k}{\int_{-\infty}^{\infty} e^{-\frac{b_k p_k^2}{xT}} dp_k} \cdot \frac{e^{-\frac{1}{xT} h'(q_{l+1}, \dots q_s, p_{m+1}, \dots p_s^b)} dq_{l+1} \dots dq_s dp_{m+1} \dots dp_s}{\int_{(\mu-(l+m))} e^{-\frac{1}{xT} h'(q_{l+1}, \dots q_s, p_{m+1}, \dots p_s, b)} dq_{l+1} \dots dq_s dp_{m+1} \dots dp_s}$$

$$dW' = \int_{(\mu-(l+m))} dW = \prod_{k=1}^{l} \frac{e^{-\frac{a_k q_k^2}{xT}} dq_k}{\int_{-\infty}^{\infty} e^{-\frac{a_k q_k^2}{xT}} dq_k} \cdot \prod_{k=1}^{m} \frac{e^{-\frac{b_k p_k^2}{xT}} dp_k}{\int_{-\infty}^{\infty} e^{-\frac{b_k p_k^2}{xT}} dp_k}$$

integracija po irelevantnim koordinatama

vjerojatnost da molekula ima koordinate između

$q_1, q_1+dq_1 \dots q_l, q_l+dq_l \quad p_1, p_1+dp_1 \dots dp_m, p_m+dp_m$

$\varepsilon_s = a_s q_s^2 \qquad \varepsilon_s = b_s p_s^2$

energije s-tih stupnjeva slobode

→ kod oscilacija imamo i jedan i drugi energ. stupanj slobode za 1 stupanj slobode dok kod translacije samo drugi (rotacije) u prvom slučaju

$$\bar{\varepsilon}_s = \int_{(\mu} a_s q_s^2 dW \qquad \bar{\varepsilon}_s = \int_{(\mu} b_s p_s^2 dW$$

$\int_{(l+m)} a_s q_s^2 dW'$

integracija po svim osalim koordinatama, dovodi do integrala koji se kate

$$\Rightarrow \quad \bar{\varepsilon}_s = \frac{\int_{-\infty}^{\infty} a_s q_s^2 e^{-\frac{a_s q_s^2}{xT}} dq_s}{\int_{-\infty}^{\infty} e^{-\frac{a_s q_s^2}{xT}} dq_s} = \frac{1}{2} xT$$

Srednja energija molekule iznosi $\frac{1}{2}xT$ po energetskom stupnju slobode

$\Rightarrow$ za osc. stupanj slobode (xT)

$$\frac{a_s q_s^2}{xT} = t^2 \qquad \sqrt{\frac{a_s}{xT}}\, q_s = t$$

$$\bar{\varepsilon}_s = \frac{\int_{-\infty}^{\infty} xT\, t^2 e^{-t^2} \sqrt{\frac{xT}{a_s}}\, dt}{\int_{-\infty}^{\infty} e^{-t^2} \sqrt{\frac{xT}{a_s}}\, dt} = xT \cdot \frac{\int_{-\infty}^{\infty} t^2 e^{-t^2} dt}{\int_{-\infty}^{\infty} e^{-t^2} dt} = xT \cdot \frac{\frac{2-1}{2}\int_{-\infty}^{\infty} e^{-t^2} dt}{\sqrt{\pi}} = xT \cdot \frac{\frac{1}{2}\sqrt{\pi}}{\sqrt{\pi}} = \frac{1}{2} xT$$

original !!!

napomene:

xxx) što se tiče granica integrala (da li su $+\infty, -\infty$) kod pot. energije harm. oscilacija pitanje je da li je $\bar{\varepsilon}_{s_{pot}} = \frac{1}{2}xT$ ili sa nekim korekcionim faktorom

→ očito moramo pribjeći idealizaciji da imamo idealan harmon. oscilator zato što za velike amplitude ili moramo zaključiti da zbog prirode kon. raspodjele (i izraza za $U_{pot}^{osc.}$) takve velike amplitude su malo vjerojatne, pa čak kod bi bile i moguće, tako da teorijska idealizacija olakšava idealizaciju

$$\Rightarrow \overline{p_i \frac{\partial H}{\partial p_i}} = \frac{1}{\beta} \frac{\int_\Gamma e^{-\beta H} d\phi_\Gamma}{\int_\Gamma e^{-\beta H(q_1,\dots p_s)} d\phi_\Gamma} = \frac{1}{\beta} = kT \qquad \forall i = 1,\dots s$$

$$\Rightarrow \underline{\bar{E}_K = s \cdot \frac{kT}{2}}$$

translac.
rotac.
oscilacije

!!! možemo čak smatrati da se tu radi o $S = s \cdot N$, tj. usrednjenje E_K (kin. energ. u Hamiltonijanu čitavog sustava) ide po čitavom Γ-prostoru sustava od N molek. i po dobro poznatoj opće kan. raspodjeli.

→ bez obzira na karakter gibanja, prosječni doprinos po stupnju slobode kinetičke energije je $\frac{1}{2}kT$

→ Teorem jednake rasp. energ. na sve stupnjeve slobode odnosi se samo na kinet. energ.

→ Proturječje klas. fizike: 1° 2-A molek. → 5 st. slobode (3 transl. & 2 rotaciona) ϑ, φ

$$\rightarrow \bar{E}_K = 5 \cdot \frac{kT}{2}$$

2° molekule razbijemo na sastavne dijelove (jezgre, elektrone) → velik broj st. slobode
mora bi voditi na veću prosj. energ. kinetičke
- u takvim slučajevima $\bar{E}_K$ neće biti determinirana
→ Q.M. - neki stupnjevi slobode imaju pridružene kvantizirane energ. nivoe i ostaju zamrznuti - ako term. energija nije dovoljno velika za pobud.
tj. imaju velik razmak između energ. stanja
⇒ ako je term. obrok kT premalen tada bi svi stupnjevi slobode bili odmrznuti. ⇒ ∄ jednoznačna vrijednost za $\bar{E}_K$

Poseban slučaj

$H = E_K + E_p$ ($T+U$) za klas. mob. & konz. sile

→ ako se (dio) pot. energija u Hamiltonijanu molekule (ili čak čitavog sustava !!!) može predočiti u obliku

$$\underline{E_p = \frac{1}{2} \sum_{i=1}^{S_{os}} q_i \frac{\partial H}{\partial q_i}}$$

gdje je S_{os} broj mogućih oscilac. st. slobode u molekuli (ili čitavom sustavu $S_{os} = s_{os} \cdot N$)

→ pot. energ. oscil. se može dako predočiti samo u slučaju harm. oscilacija

h-ta molekula $U_h^{osc.} = \sum_{k=1}^{S_{os}} \frac{4\pi^2 m_{hk} \nu_{hk}^2 \cdot \lambda_{hk}}{2}$. m_{hk} - masa k-tog atoma u h-toj molek

$U^{os.} = \sum_{h=1}^{N} U_h^{osc.}$

nakon što do shvatimo kao gen. koord. Q_i

$U^{os.} = E_p = \sum_{i=1}^{S_{os}} \sum_{j=1}^{S_{os}} C_{ij} Q_i Q_j$, konstante

ustvari suma po kombinacijama s ponavljanjem ⇒

⇒ mora biti $C_{ij} = C_{ji} = \frac{1}{2} C_{ij} = \frac{1}{2} C_i$

analogno ranijem

$\Rightarrow \frac{\partial E_p}{\partial Q_i} = 2 \sum_{j=1}^{S_{os}} C_{ij} Q_j$

hamiltonijan h-te molek. $H_h = [T_h + T_{h_{rot}} + T_{h_{osc.}}] + [U_{vh} + \underbrace{U_h^{osc.}}_{= E_{p_h}} + U_{h\,int}]$ $\quad H = \sum_{h=1}^{N} H_h$

⇒ od gen. koordinata Q_i $i = 1, \dots S_{os}$ (može i $S_{os} = S_{os} \cdot N$) ovisi samo E_{p_h}, dok

$T_{h_{osc.}}$ ovisi samo o $\dot{Q}_i$, jer $Q_{ij} = \text{const.}$ budući ne uvodimo polarni sustav (gen. koordinata)

kao u slučaju transl. ili rotac. gibanja (Euler. kutevi) *)

$\Rightarrow \frac{\partial H}{\partial Q_i} = \frac{\partial E_p}{\partial Q_i} \quad \forall i = 1, \dots S_{os}$ (može i $S_{os} = S_{os} \cdot N$)

$\Rightarrow \underline{\sum_{i=1}^{S_{os}} Q_i \frac{\partial H}{\partial Q_i} = \sum_{i=1}^{S_{os}} Q_i \frac{\partial E_p}{\partial Q_i} = \sum_{i=1}^{S_{os}} Q_i \cdot 2 \sum_{j=1}^{S_{os}} C_{ij} Q_j = 2 \sum_{i=1}^{S_{os}} \sum_{j=1}^{S_{os}} C_{ij} Q_i Q_j = 2E_p}$

$\bar{E}_p = \frac{1}{2} \sum_{i=1}^{S_{os}} \overline{Q_i \frac{\partial H}{\partial Q_i}}$

(može i $S_{os} = S_{os} \cdot N$ i tada usrednjavamo po kan. raspodjeli cijelog Γ-prostora, a ne uz uvjet **) po kan. raspodjeli q_i-prostora)

$\overline{Q_i \frac{\partial H}{\partial Q_i}} = \frac{\int_{\mu} \int_{\Gamma} Q_i \frac{\partial H}{\partial Q_i} e^{-\beta H(Q_1, \dots p_s)} d\phi_\mu}{\int_{\mu} \int_{\Gamma} e^{-\beta H(Q_1, \dots p_s)} d\phi_\Gamma} = \frac{\left(-\frac{1}{\beta}\right) \int_{(\mu - Q_i)} \left[\int_{Q_{i\,min}}^{Q_{i\,max}} Q_i \frac{\partial}{\partial Q_i} e^{-\beta H} dQ_i \right] d\phi'}{\int_{\mu} e^{-\beta H} d\phi_\mu}$

pravilo računanja integr. za kon. integr.

$\int_{Q_{i\,min}}^{Q_{i\,max}} \underbrace{Q_i}_{u} \underbrace{\frac{\partial}{\partial Q_i} e^{-\beta H(Q_1, \dots p_s)} dQ_i}_{dv} = \underbrace{\left[Q_i e^{-\beta H(Q_1, \dots p_s)} \right]_{Q_{i\,min}}^{Q_{i\,max}}}_{uv} - \int_{Q_{i\,min}}^{Q_{i\,max}} e^{-\beta H(Q_1, \dots p_s)} dQ_i$

Kartezijeve koordinate: jer druge u tom slučaju nema potrebe niti uvoditi zbog *)

$Q_{i_{min}} = -\infty \quad H = \sum_i c_{ij} Q_i^2 \Rightarrow H = \infty$

$Q_{i_{max}} = +\infty \quad H = \sum_i c_{ij} Q_i^2 \Rightarrow H = \infty$

& $\lim_{x \to \infty} x e^{-x} = 0$

uz napomenu **) vidi (26)

$$\Rightarrow \overline{q_i \frac{\partial H}{\partial q_i}} = \frac{1}{\beta} \frac{\int_{\mu} e^{-\beta H} d\phi}{\int_{\mu} e^{-\beta H} d\phi} = \frac{1}{\beta} = kT \qquad \forall\, i = 1, \dots S_{os} \quad (\text{tj. } S_{os} = s_0 \cdot N)$$

$$\Rightarrow \underline{\bar{E}_p = S_{os} \cdot \frac{kT}{2}} \qquad (\text{tj. } S_{os} = s_0 \cdot N)$$

1. Primjer H.O.

$$H = \sum_{i=1}^{S_{os}} \frac{p_i^2}{2m} + \sum_{i=1}^{S_{os}} \frac{m\omega^2 q_i^2}{2} \qquad (p_i^2,\ q_i^2)$$

$$p \frac{\partial H}{\partial p} = p \cdot \frac{p}{m} = \frac{p^2}{m}$$

$$q \frac{\partial H}{\partial q} = q \cdot m\omega^2 q = m\omega^2 q^2$$

$$\Rightarrow H = \frac{1}{2} \sum_{i=1}^{S_{os}} \left(p_i \frac{\partial H}{\partial p_i} + q_i \frac{\partial H}{\partial q_i} \right) \qquad S = S_{os} \cdot N$$

prema ćirdavoj Γ

$$\underline{\bar{E}^{os.} = \bar{H}^{os.} = \frac{1}{2} \sum_{i=1}^{S_{os}} \left(p_i \overline{\frac{\partial H}{\partial p_i}} + q_i \overline{\frac{\partial H}{\partial q_i}} \right) = \frac{1}{2} S (kT + kT) = kT \cdot S_{os.}}$$

→ **prosjeèna vrijednost pot. i kin. energije je ista za harm. oscilator**
to slijedi i iz klas. razmatranja

$$m\ddot{q} = -kq \qquad k = m\omega^2 \qquad t=0 \quad q=0 \quad \dot{q}=v$$
$$\beta = 0 \qquad A = \frac{v}{\omega}$$

$$q = A \sin \omega t$$
$$\dot{q} = A\omega \cos \omega t$$

Kin. energija $\quad \frac{p^2}{2m} = \frac{m\dot{q}^2}{2} = \frac{m\omega^2 A^2}{2} \cos^2 \omega t$

pot. energija $\quad \frac{m\omega^2 q^2}{2} = \frac{m\omega^2 A^2}{2} \sin^2 \omega t$

! zalkan pokaže rasp. energije primjenjen na atom - na drugi način.

$$\bar{E}_k = \frac{1}{\tau} \int_0^{\tau} \frac{p^2}{2m} dt = \frac{m\omega^2 A^2}{2\tau} \cdot \left(\frac{t}{2} + \frac{1}{4\omega} \sin 2\omega t \right) \Big|_0^{\tau} = \frac{m\omega^2 A^2}{4}$$

$$\bar{E}_p = \frac{1}{\tau} \int_0^{\tau} \frac{m\omega^2 q^2}{2} = \frac{m\omega^2 A^2}{2\tau} \left(\frac{t}{2} - \frac{1}{4\omega} \sin 2\omega t \right) \Big|_0^{\tau} = \frac{m\omega^2 A^2}{4}$$

$\Big\} (=)$

$\omega = \frac{2\pi}{\tau}$

$\Rightarrow E_k$ & E_p usrednjeni po vremenu (po periodu) daju isto, kao i usklađaju primjena klas. raspodjele

nije ni čudo kad je pri izvođenju kanonske raspodjele upotrebljena klasična hipoteza

Kopa Kaže: nakon dovoljno dugog vremena fazna trajektorija dobro prolazi blizu bilo kojoj fazno točci.

$\Rightarrow \langle q \rangle = \bar{q}$

Virijalni teorem

Def: virijala $\underset{S}{\mathcal{V}} = \sum_{i=1}^{S} q_i F_i$ — q_i: gen. koord., F_i: gen. sila; $S = s \cdot N$

$$F_i = \dot{p}_i = -\frac{\partial H}{\partial q_i} \Rightarrow \underset{S}{\mathcal{V}} = -\sum_{i=1}^{S} q_i \frac{\partial H}{\partial q_i}$$

$\overline{q_i \frac{\partial H}{\partial q_i}}$ po Γ prostoru $= kT$

→ jednoatomni plin od N čestica (može i 2-A)

$S = 3N$ ($S \cdot N$ (+ rotacija)) $\Rightarrow \underset{3N}{\mathcal{V}} = -3NkT$

u tom istom sistemu $\bar{E}_K = \frac{3N}{2} kT$

$\Rightarrow \boxed{\bar{\mathcal{V}} = -2\bar{E}_K}$ Clausius-ov virijalni tm.

→ iz virijalnog tm. možemo izvesti jbu stanja realnog plina

specijalno: idealni plin

$H(q_1, \dots p_{3N}) = H = \sum_{h=1}^{N} [T_h + T_{hrot} + T_{hos.} + U_{Vh} + U_{h_{os.}} + U_{h_{int}}] + H_{ext.s\ tenzost.}(V)$

T_h: ne ovisi o gen. koord.; $a \equiv V$ — vanjski parametar koji uključuje oblik i zapreminu posude

sile na molekule: 1° međumolekularne
2° stijenke posude djeluju prisilom na molek. → -tlak

proradi

? $\mathcal{V} = \mathcal{V}_1 + \mathcal{V}_2$

$\mathcal{V}_1$: interakcija molekula; $\mathcal{V}_2$: interakcija sa stijenkama posude

$\mathcal{V}_1 = \sum q_i K_i$ — zanemarivo za idealni plin

$\Delta\vec{F} = S\Delta F_x \vec{i}$

$\lim_{n\to\infty} \sum_{i=1}^{n} S x \cdot \Delta F_x$ — raspodjeljena ploha

$\bar{\mathcal{V}}_2 = \int \vec{r}\, d\vec{F}$ ($S x\, dF_x$) — dominantno za molekule uz stijenke

po površini u blizini gran. posude — plošni integral

$d\vec{F} = -P \cdot d\vec{f}$ — def. tlak. plohe

tlak je konst. (svuda je) jer prom. term. uravnotežen sistem

$\bar{\mathcal{V}}_2 = -P \iint \vec{r}\, d\vec{f} = -P \int_V \underbrace{\mathrm{div}\, \vec{r}}_{3}\, d\tau = -3PV_{posude}$ ($S x df_x$)

po površini u blizini gran. posude

$d\vec{f} = S df_x \vec{i}$

može i S: $-3NkT = \bar{\mathcal{V}}_1 - 3PV \Rightarrow \boxed{PV = NkT + \frac{1}{3}\bar{\mathcal{V}}_1}$ — može i $\frac{S}{3}$

↓ naziv u termodinamici

Virijalni članovi razvoja

1-A plin $\quad \mathcal{V}_S = \sum_{i=1}^{S} \mathcal{Z}_i F_i$

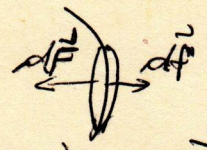
$\mathcal{V} = \mathcal{V}_1 + \mathcal{V}_2$ posod

$\mathcal{V} = -\sum_{i=1}^{S} \mathcal{Z}_i \frac{\partial H}{\partial \mathcal{Z}_i} \qquad F_i = -\frac{\partial H}{\partial \mathcal{Z}_i}$

$\bar{\mathcal{V}} = -S\,\frac{1}{2}kT = -S\,\frac{1}{2}NkT = -2\bar{E}_K$

$H = E_K + E_p$

$\bar{\mathcal{V}}_2 = \int_P \vec{r}\, d\vec{F}$



$d\vec{F} = -P\,d\vec{f}$

$= -P \int_P \vec{r}\, d\vec{f} = -P \int_V \mathrm{div}\,\vec{r}\, dV = -3PV$

$\bar{\mathcal{V}}_2 = \sum_{i=1}^{S} \mathcal{Z}_i F_{i\,stij.}$ na i-to vrsto sil. v čvrsti snovi

$U_{ind.\,ter.}$ na gromici razsiti $\begin{cases} 0 & \text{v notranjosti } V \\ \infty & \text{na gromici} \end{cases}$

simetrijo po indek. porpelom kolonam

$= \sum_{i=1}^{S}{}' \mathcal{Z}_i F_{i\,stij.}$ simetrijo po plohi.

$= \sum_{i=1}^{S}{}' \mathcal{Z}_i \Delta F_{i\,stij.} = \oint_P \vec{r}\, d\vec{f}$

Kadbi ∃ vanjsko polje - sigurno deformacija pasudi ⇒ bi bilo suvoplje redi

Vanj. polja nema - $\mathcal{Z}_i$ - samo kvadratne kvant. kord.

$\mathcal{V}_1 = \sum_i \mathcal{Z}_i \mathcal{K}_i$

$-3NkT = \bar{\mathcal{V}}_1 - 3PV$

$PV = NkT + \frac{1}{3}\bar{\mathcal{V}}_1$

$\mathcal{V}_S = \sum_{i=1}^{S} \mathcal{Z}_i F_i$ 1-A plin $S = 3N$

$H = \sum_{h=1}^{N} T_h + U_{int} + U_{h\,int} + U_{h\,int\,ter}$

$\vec{F}_{h\,calm} = -\mathrm{grad}_h (U_{int}) + \vec{F}_{h\,stijna} = -\mathrm{grad}_h (U_{ind.\,ter.})$

$-S\frac{\partial U_{int}}{\partial x_h}\vec{i} \qquad -S\frac{\partial U_{ind.\,ter.}}{\partial x_h}\vec{i}$

$\mathcal{V}_S = -\sum_{i=1}^{S} \mathcal{Z}_i \frac{\partial H}{\partial \mathcal{Z}_i}$

$= -\sum_{i=1}^{S} \mathcal{Z}_i \frac{\partial U_{ind}}{\partial \mathcal{Z}_i} - \sum_{i=1}^{S} \mathcal{Z}_i \frac{\partial U_{int}}{\partial \mathcal{Z}_i}$

$\Rightarrow \frac{\partial H}{\partial \mathcal{Z}_i} = \frac{\partial U_{int}}{\partial \mathcal{Z}_i} + \frac{\partial U_{ind\,ter.}}{\partial \mathcal{Z}_i}$

$= \mathcal{V}_1 + \mathcal{V}_2$

$\mathcal{V}_1 = \sum \mathcal{Z}_i \mathcal{K}_i \qquad \mathcal{K}_i = -\frac{\partial U_{int}}{\partial \mathcal{Z}_i}$

$\Rightarrow F_i = -\frac{\partial U_{int}}{\partial \mathcal{Z}_i} - \frac{\partial U_{ind\,ter.}}{\partial \mathcal{Z}_i} = -\frac{\partial H}{\partial \mathcal{Z}_i}$

$F_i = \mathcal{K}_i + F_{i\,stijna}$

Interpolacija na površini - na gromici volum

$\int \mathcal{Z}_i \quad i = 1, \ldots S$

to delo!!!

→ plin N-čestica & δ st. slobode $S = s \cdot N$

$$\mathcal{V} = \sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_i$$

$\vec{F}_i$ – generaliz. sila koja djeluje na i-tu česticu, koju možemo rastaviti na dva dijela

1. dio su sile koje dolaze od djelovanja drugih čestica na i-tu
2. dio je sila koja dolazi od posude

$$\vec{F}_i = \vec{F}_{i\,int}(N-1) + \vec{F}_{i\,posude} \quad \Rightarrow \quad \mathcal{V} = \underbrace{\sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_{i\,int}}_{\mathcal{V}_1} + \underbrace{\sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_{i\,posude}}_{\mathcal{V}_2}$$

E_p $\quad$ $\vec{K}_i$

$H = E_k + (U_{int} + U_{int\,pos})$ & $F_i = F_{i\,int} + F_{i\,posude} \Rightarrow \frac{\partial H}{\partial z_i} = \frac{\partial U_{int}}{\partial z_i} + \frac{\partial U_{int\,pos}}{\partial z_i}$ $\quad i = 1, \dots S$

$\vec{K}_{ni} = -\frac{\partial U_{int}}{\partial \vec{z}_i}$

$$\vec{r}_i \cdot \vec{F}_i = -\left(x_i \frac{\partial E_p}{\partial x_i} + y_i \frac{\partial E_p}{\partial y_i} + z_i \frac{\partial E_p}{\partial z_i} \right)$$

(*) $\vec{F}_{i\,posude}$ izrazit samo na stijenki – na gran. površini

→ kako kin. energ. ne ovisi o x, y, z

$H = E_k + E_p \qquad E_p = U_{int} + U_{int\,posude}$

$$\mathcal{V} = -\sum_{i=1}^{N} \left(x_i \frac{\partial H}{\partial x_i} + y_i \frac{\partial H}{\partial y_i} + z_i \frac{\partial H}{\partial z_i} \right)$$

$$\overline{z_i \frac{\partial H}{\partial z_i}} = kT$$

po klas. analogiji

$$\overline{\mathcal{V}} = -3NkT$$

za 1-A plin. $\overline{E_k} = 3N\frac{kT}{2}$ $\Rightarrow$ $\overline{\mathcal{V}} = -2\overline{E_k}$ Clausius

$\mathcal{V} = \mathcal{V}_1 + \mathcal{V}_2$

$$\overline{\mathcal{V}_1} = \sum_{i=1}^{N} \overline{\vec{r}_i \cdot \vec{K}_i} \quad \text{interakcija}$$

sila s kojom ostale molekule djeluju na i-tu

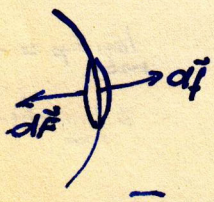
$$\mathcal{V}_2 = \sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_{i\,posude}$$

$$\overline{\mathcal{V}_2} = \sum_{i=1}^{N} \vec{r}_i \, \vec{F}_{i\,posude} \overset{*}{=} \sum_{j=1}^{N'} \overline{\vec{r}_j \, \vec{F}_{j\,posude}}$$

sumacija samo po molekulama koje su tik uz gran. plohu, a inače je $N' \ll N$

$$= \oint_{\Omega} \vec{r} \cdot d\vec{F}$$

jasno da tu doprinose samo infinitezimalni volumeni molekula uz samu gr. površ. Ω i možemo zamijeniti integraciju po svim infinitezimalnim volumenima na P, kojima pripada i infinitezimalna sila $d\vec{F}$



$d\vec{F} = -P\,d\vec{f}$ sila koja djeluje (djelić infinitezimalne molekule) da izađe iz posude i zadovolji smjer prema unutra

$$\overline{\mathcal{V}_2} = -P \int_{\Omega} \vec{r} \cdot d\vec{f} = -P \int_{V} \underbrace{\mathrm{div}\,\vec{r}}_{3} \cdot dV = -3PV_{posude}$$

$-3NkT = \overline{\mathcal{V}_1} - 3PV$

$$\Rightarrow \quad PV = NkT + \frac{1}{3}\overline{\mathcal{V}_1}$$

pretp: ℓ imamo dosta razrjed. plin ⇒ interakcija čestica nije previše velika

$$\overline{\mathcal{V}_1} = \sum_{i=1}^{N} \overline{\vec{r}_i \cdot \vec{K}_i}$$

ℓ 1-A plin & N jedn. čestica → mana rot. niti · oscilacija

$f(r)$

ℓ E_p koja opisuje međudjel. čest. → sferno-sim. fja.

tj. $E_p = f(r)$ pot. energ. čestice spram jedne druge

$\vec{\nabla}$ ↔ molek. oko sebe stvara polje sile ovisno samo o r

$U_{jh}(r_{jh}) = E_p(r_{jh})$

$\vec{F}_{jh} = -\text{grad}_h\, U_{jh}(r_{jh})$

$\vec{r}_{jh} = \vec{r}_h - \vec{r}_j$

$\vec{F}_{jh} = -\text{grad}_h\, E_p(r_{jh})$

$= -\vec{r}_{0jh} \cdot \frac{dE_p(r_{jh})}{dr_{jh}}$

$+\text{grad} = \vec{r}_0 \frac{\partial}{\partial r} + \vec{\vartheta}_0 \frac{1}{r}\frac{\partial}{\partial \vartheta} + \vec{\varphi}_0 \frac{1}{r \sin\vartheta}\frac{\partial}{\partial \varphi}$

$\vec{r}_{0jh}$ ide od j-te molek. ka h-toj, gdje djeluje sila $\vec{F}_{jh}$

$$\overline{\mathcal{V}_1} = \sum_{i=1}^{N} \overline{\vec{r}_i \cdot \vec{K}_i} =$$

(*) $\vec{F}_{hh} = 0 \qquad \vec{F}_{jh} = -\vec{F}_{hj}$

$$\sum_{h=1}^{N} \vec{r}_h \cdot \vec{K}_h = \sum_{h=1}^{N} \vec{r}_h \left(\sum_{j=1}^{N} \vec{F}_{jh}\right) = \sum_{h=1}^{N}\sum_{j=1}^{N} \vec{r}_h \cdot \vec{F}_{jh} = \frac{1}{2}\sum_{h=1}^{N}\sum_{j=1}^{N} \left(\vec{r}_h \cdot \vec{F}_{jh} + \vec{r}_j \vec{F}_{hj}\right) =$$

$$= \frac{1}{2}\sum_{h=1}^{N}\sum_{j=1}^{N} (\vec{r}_h - \vec{r}_j)\vec{F}_{jh} = \frac{1}{2}\sum_{h=1}^{N}\sum_{j=1}^{N} \vec{r}_{jh} \cdot \vec{F}_{jh} = \frac{1}{2}\sum_{h=1}^{N}\sum_{j=1}^{N} -\vec{r}_{jh} \cdot \vec{r}_{0jh} \cdot \frac{dE_p(r_{jh})}{dr_{jh}} =$$

$$= -\frac{1}{2}\sum_{h=1}^{N}\sum_{j=1}^{N} r_{jh} \cdot \frac{dE_p(r_{jh})}{dr_{jh}}$$

gdje za $j = h$ $\vec{F}_{jh} = 0$ $\left(\frac{dE_p(r_{jh})}{dr_{jh}} = 0\right)$ & $r_{jh} = 0$

$$\Rightarrow \sum_{h=1}^{N} \overline{\vec{r}_h \cdot \vec{K}_h} = -\frac{1}{2}\sum_{h=1}^{N}\sum_{j=1}^{N} \overline{r_{jh} \frac{dE_p(r_{jh})}{dr_{jh}}} = -\frac{1}{2} N(N-1)\, \overline{r \cdot \frac{dE_p}{dr}}$$

$$\boxed{\overline{\mathcal{V}_1} = -\frac{N(N-1)}{2}\, \overline{r\frac{dE_p}{dr}} \approx -\frac{N^2}{2}\, \overline{r\frac{dE_p}{dr}}} \qquad \text{za } N \gg 1$$

(*) ne ∃ $\vec{F}_h$ od vanj. polja, smatrano da ga nema, inače P nabi bio smuda ist. i nebi mogli lako izračunati $\overline{\mathcal{V}_2}$

→ E_p opisuje pot. energiju između dvije čestice

na tri papira razrađeno napotp.

$$\overline{r\frac{dE_p}{dr}} \overset{?}{=} \frac{1}{V}\int r\frac{dE_p}{dr} e^{-\beta E_p} d^3r = \frac{4\pi}{V}\int_0^\infty \frac{dE_p}{dr} \cdot r^3 e^{-\beta E_p} dr$$

na papiru ③ izvršena aprox. $e^{-\beta E_p(r)} \approx 1$ u Kanonskoj raspodjeli u nazivniku

$$= \frac{4\pi}{V} \cdot \frac{1}{\beta}\int_0^\infty r^3 d\left(1 - e^{-\beta E_p}\right)$$

→ da olakšamo integraciju uzimamo Kuglu koja se proteže u ∞

$$= \frac{4\pi KT}{V}\left\{\left[r^3\left(1 - e^{-\beta E_p}\right)\right]_0^\infty - 3\int_0^\infty r^2\left(1 - e^{-\beta E_p}\right)dr\right\} =$$

$\lim_{r\to\infty} E_p = -0$

& $\lim_{x\to\infty} x\left(1 - e^{-\frac{1}{x}}\right) = 0$

$$= -3\,\frac{4\pi KT}{V}\int_0^\infty \left(1 - e^{-\beta E_p}\right) r^2 dr$$

$$= -\frac{3KT}{V} \cdot 2B(T) \qquad 2 \cdot B(T) = 4\pi\int_0^\infty \left(1 - e^{-\beta E_p}\right) r^2 dr$$

$$\Rightarrow \boxed{\overline{\mathcal{V}_1} = 3 \cdot \frac{N^2}{2} \cdot \frac{KT}{V} \cdot 2B = 3\,\frac{N^2 KT B}{V}}$$

$$\sum_{i=1}^{s} p_i \frac{\partial H}{\partial p_i} \dot{q}_i = \sum \frac{\partial E_k}{\partial q_i} \dot{q}_i = \dot{E}_k$$

$$p_i \frac{\partial H}{\partial p_i} = kT$$

1. DHO:

$$H = \frac{p^2}{2m} + \frac{m\omega^2 q^2}{2}$$

$$p \frac{\partial H}{\partial p} = p \cdot \frac{p}{m} \qquad q \frac{\partial H}{\partial q} = q \cdot m\omega^2 q \Rightarrow H = \frac{1}{2}\left[p \frac{\partial H}{\partial p} + q \cdot \frac{\partial H}{\partial q}\right]$$

$$V = \sum_{i=1}^{N} \vec{r}_i \cdot \vec{F}_i \qquad \vec{F}_i = -\operatorname{grad}_i \cdot E_p = -\operatorname{grad}_i \cdot E_{kin} = -\operatorname{grad}_i H$$

$$= -\sum_{i=1}^{N} \delta' x_i \frac{\partial H}{\partial x_i}$$

$$\vec{F}_i = \vec{K}_i + \vec{F}_{i\,pomoc}$$

$$\overline{V} = -3NkT$$

$$V = V_1 + V_2 \qquad V_1 = \sum_{i}^{N} \vec{r}_i \cdot \vec{K}_i \qquad V_2 = \sum_{i=1}^{N} \vec{r}_i \vec{F}_{i\,pom}$$

$$\vec{V}_2 = \sum_{i=1}^{N} \vec{r}_i \cdot F_{i\,pom} = \sum_{i=1}^{N'} \vec{r}_i \cdot \vec{F}_i \quad \Big| \to dS, \; d\vec{F} = -p\,d\vec{f}$$

$$= \int_{\Omega} \vec{r} \cdot d\vec{F} = -p \int_{\Omega} \vec{r} \cdot d\vec{f} = -3pV$$

$$\sum_{h=1}^{N} \vec{r}_h \cdot \vec{F}_h = \sum_{h=1}^{N} \vec{r}_h \cdot \left(\sum_{g=1}^{N} \vec{F}_{gh} \right) = \frac{1}{2} \sum_{h}^{N} \sum_{g}^{N} \vec{r}_{gh} \cdot \vec{F}_{gh}$$

$\vec{F}_{hh} = 0$

$$\vec{F}_{gh} = -\vec{r}_{gh} \frac{dE_p(r_{gh})}{dr_{gh}}$$

$$= +\frac{1}{2} \sum \sum \vec{r}_{gh} \cdot (-\vec{r}_{gh}) \frac{dE_p(r_{gh})}{dr_{gh}}$$

$$= -\frac{1}{2} \sum \sum r_{gh} \cdot \frac{dE_p(r_{gh})}{dr_{gh}}$$

$$\sum_{h=1}^{N} \vec{r}_h \vec{F}_h = \frac{1}{2} \sum \sum \overline{r_{gh} \frac{dE_p(r_{gh})}{dr_{gh}}}$$

$$= -\frac{N(N-1)}{2} \overline{r \frac{dE_p(r)}{dr}}$$

$H = E_{kin} + E_p$

$$\overline{r_{gh} \cdot \frac{dE_p(r_{gh})}{dr_{gh}}} = \frac{\iint r_{gh} \frac{dE_p(r_{gh})}{dr_{gh}} e^{-\beta E_p(r_{gh})} d^3\vec{r}_g \, d^3\vec{r}_h}{\iint e^{-\beta E_p(r_{gh})} d^3\vec{r}_g \, d^3\vec{r}_h}$$

$\vec{r}_{gh} = \vec{r}_h - \vec{r}_g \qquad \vec{R} = \frac{\vec{r}_h + \vec{r}_g}{2}$

$d^3\vec{r}_{gh} \, d^3\vec{R}$

$$= \frac{\iint r_{gh} \frac{dE_p(r_{gh})}{dr_{gh}} e^{-\beta E_p(r_{gh})} d^3\vec{r}_{gh}}{\iint e^{-\beta E_p(r_{gh})} d^3\vec{r}_{gh}}$$

$e^{-\beta E_p(r_{gh})} \approx 1$

$- \frac{E_p}{kT} \ll 1 \approx 0$

$e^{-\beta E_p(r_{gh})} \approx 1$

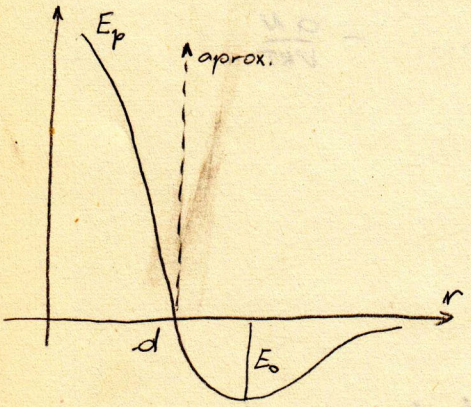
(28) b)

$$\Rightarrow \quad PV = NKT + \frac{N^2 KT B}{V}$$

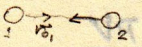
$$\underline{PV = NKT\left(1 + \frac{N}{V}B(T)\right)} \quad + \left(\frac{N}{V}\right)^2 C$$

$B(T)$ – drugi virij. koef.

→ razvoj P po potenc. gustoće (prema 1° gustoća mala → lin. član)



1. na malim udalj. jake odbojne sile $\quad \vec{F}_{12} = -\,\mathrm{grad}E_p = -\vec{r}_{01}\frac{dE_p}{dr}$



2. na većim udalj. sile su privlačne

E_0 – dubina potenc. jame

$$B = 2\pi \int_0^\infty (1 - e^{-\beta E_p}) r^2 dr$$

$$B(T) = 2\pi \left[\int_0^d r^2 dr \; - \frac{1}{KT} \cdot KT \int_d^\infty (e^{-\beta E_p} - 1) r^2 dr \right]$$

$$\underline{B = b - \frac{a}{KT}} \qquad \underline{b = \frac{2\pi d^3}{3}} \quad \text{neovisan o } T \qquad \underline{a = 2\pi KT \int_d^\infty (e^{-\beta E_p} - 1) r^2 dr} \quad \text{ovisan o } T$$

→ $a > 0$ jer za $r \in (d, \infty)$ $E_p < 0$ $\quad e^{(-1)} \geq 1 \quad \Rightarrow \int_d^\infty > 0$

→ da li prevladava član ovisan o T ili onaj neovisan o T

→ $\underline{KT \gg |E_p|}$ za $\forall\, r \in (d, \infty) \quad \Rightarrow KT \gg |E_0|$

$$\Rightarrow e^{-\beta E_p} \approx 1 - \frac{E_p}{KT} \qquad \Rightarrow \quad -a = -2\pi \int_0^\infty E_p(r)\, r^2 dr$$

E_p mora (iz matem. razloga – jer privlačna interakcija proizlazi iz dipolne interakcije) brzo dešit. nul.

$$\underline{E_p = -\frac{C}{r^n}} \qquad n > 3 \qquad n = 6$$

$\Rightarrow$ u modelu visokih temp. a neovisan o T

$v = \frac{V}{n}$

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

$$\frac{PV}{NKT} = 1 + \frac{N}{V}\left(b - \frac{a}{kT}\right)$$

$R = \tilde{N}k \Rightarrow nR = n\tilde{N}k = Nk$

→ iz Van der Waalsove jbe. $\cdot \left(P + \frac{aN^2}{V^2}\right)\left(V - b\frac{N}{V}\right) = NkT$

$$PV + \frac{aN^2}{V} = \frac{NkT}{1 - \frac{bN}{V}}$$

$$\frac{PV}{NkT} = \frac{1}{1 - \frac{bN}{V}} - \frac{aN^2}{NVkT} = 1 + \frac{bN}{V} + \left(\frac{bN}{V}\right)^2 + \ldots - \frac{aN}{VkT}$$

$$\frac{PV}{NkT} = 1 + \frac{N}{V}\left(b - \frac{a}{kT}\right) + b^2\left(\frac{N}{V}\right)^2 + \ldots$$

→ slaganje $\mathcal{F}$ do kon. čvrstog gustoće

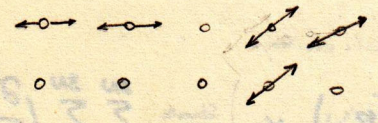
Koje sve pretp. moramo primijeniti da bismo došli do ovakvog slaganja

na udaljenosti r_0 mora doći do naglog skoka potencijala ⇒ F ovelika odbojna

Titranje čvrstog tijela

amorfna

Kristali - atomi smješteni pravilno u čvorištu kristalne rešetke → min. pot. energ.



- oscilacije reda s temp, za male temp. amplit. oscil. male
Kod dovoljno temp → taljenje
- kristalna rešetka regulira raspored čvorišta

amorfna tijela - nasumce razbacana čvorišta, jer je veliko relaksacijsko vrijeme (vrijeme poprimanja pravilnog rasporeda čvorišta)

- srednja energija kristala i **dopunski kapacitet** ?

Pretp: temp. $\ll$ temp. tališta $\Rightarrow$ lokalizacija atoma i male amplitude titr. oko položaja ravnoteže

$\Rightarrow$ pot. energ. razvijemo u Tayl. red po amplitudama i zadržimo samo prve članove

N-atoma $x_i \quad i = 1, 2, \dots 3N$

lokalna koord. za k-atom tj. mjerena u lokal. koord. sustavu $x_{ri} = 0$ položaj ravnoteže

Klas. mech. & Vanz. sile $\Rightarrow H = T + U = E_K(\dot{x}_1, \dots \dot{x}_{3N}) + E_p(x_1, \dots x_{3N})$

$\bar{C}_n^k = \binom{n+k-1}{k}$ $\bar{C}_m^n$ broj članova

$$u(x_1+h_1, \dots, x_m+h_m) = u(x_1, \dots x_m)_{(x_1, \dots x_m)} + \sum_{s=1}^{n-1} (h_1 u_{x_1} + \dots + h_m u_{x_m})^{(s)}_{(x_1, \dots x_m)} \cdot \frac{1}{s!} + \frac{1}{n!} (h_1 u_{x_1} + \dots + h_m u_{x_m})^{(n)}_{x_1+\theta h_1, \dots x_m+\theta h_m}$$

$$E_p(x_1, \dots x_{3N}) = E_p(0) + \frac{1}{1!} \sum_{i=1}^{3N} \left(\frac{\partial E_p}{\partial x_i}\right)_0 x_i + \quad 0 \equiv (0, 0, \dots 0)$$

$$+ \frac{1}{2} \sum_{i,j=1}^{3N} \left(\frac{\partial^2 E_p}{\partial x_i \partial x_j}\right)_0 x_i x_j + \dots \qquad \bar{C}_{3N}^2 = \binom{3N+2-1}{2} = \frac{3N(3N+1)}{2}$$

$$\sum_{i,j=1}^{3N} = \sum_{i=1}^{3N} \sum_{j=1}^{3N}$$

ali kad se dobije permutacija istih predstavnika zbroje

$\sum_{i,j=1}^{3N} = 2 \sum_{i \le j=1}^{3N}$ posuma kombinacij. od $3N$ elem. 2 reda

opć. $F_i(x_1, \dots x_{3N})$, ali: $F_i(x_i)$

$$\left(\frac{\partial E_p}{\partial x_i}\right)_0 = (-F_i)_0 = 0 \qquad \text{jer sila u položaju ravnoteže ne } \exists$$

$$\Rightarrow E_p(x_1, \dots x_{3N}) \approx \underbrace{E_p(0, \dots 0)}_{E_p(0)} + \frac{1}{2} \sum_{i=1}^{3N} \sum_{j=1}^{3N} \left(\frac{\partial^2 E_p^{(x_1, \dots x_{3N})}}{\partial x_i \partial x_j}\right)_{0, \dots 0} x_i x_j$$

$$\Rightarrow \frac{\partial E_p}{\partial x_l} \approx 0 + \frac{1}{2} \frac{\partial}{\partial x_l} \sum_{i=1}^{3N} \sum_{j=1}^{3N} \left(\frac{\partial^2 E_p}{\partial x_i \partial x_j}\right)_0 x_i x_j$$

$l = 1, \dots 3N$

$$\sum_{i=1}^{3N}\left(x_\ell\left(\frac{\partial^2 E_p}{\partial x_i \partial x_\ell}\right)_0 x_i + \sum_{\ell\neq j=1}^{3N}\left(\frac{\partial^2 E_p}{\partial x_i \partial x_j}\right)_0 x_i x_j\right) \qquad x_\ell \sum_{i=1}^{3N}\left(\frac{\partial^2 E_p}{\partial x_i \partial x_\ell}\right)_0 x_i$$

originalno !!!

$$\frac{\partial E_p(x_1,\dots x_{3N})}{\partial x_\ell} = \frac{1}{2}\frac{\partial}{\partial x_\ell}\left[\sum_{\ell\neq i=1}^{3N}\sum_{\ell\neq j=1}^{3N}\left(\frac{\partial^2 E_p}{\partial x_i \partial x_j}\right)_0 x_i x_j + x_\ell^2\left(\frac{\partial^2 E_p}{\partial x_\ell^2}\right)_0 + x_\ell \sum_{\ell\neq i=1}^{3N}\left(\frac{\partial^2 E_p}{\partial x_i \partial x_\ell}\right)_0 x_i + x_\ell \sum_{\ell\neq j=1}^{3N}\left(\frac{\partial^2 E_p}{\partial x_\ell \partial x_j}\right)_0 x_j\right]$$

$$= \frac{1}{2}\left[0 + 2x_\ell\left(\frac{\partial^2 E_p}{\partial x_\ell^2}\right)_0 + \sum_{\ell\neq j=1}^{3N}\left[\underbrace{\left(\frac{\partial^2 E_p}{\partial x_j \partial x_\ell}\right)_0 + \left(\frac{\partial^2 E_p}{\partial x_\ell \partial x_j}\right)_0}_{2\left(\frac{\partial^2 E_p}{\partial x_j \partial x_\ell}\right)_0}\right] x_j\right] \overset{\text{Schwartz.}}{=}$$

$$= \sum_{j=1}^{3N}\left(\frac{\partial^2 E_p}{\partial x_j \partial x_\ell}\right)_0 x_j$$

$H = E_K(\dot{x}_1,\dots \dot{x}_{3N}) + E_p(x_1,\dots x_{3N})$ — jer nema rot., transl. gibanja čestica sustava oscilacija

$$\Rightarrow \sum_{i=1}^{3N} x_i \frac{\partial H}{\partial x_i} = \sum_{i=1}^{3N} x_i \frac{\partial E_p}{\partial x_i} = \sum_{i=1}^{3N} x_i \left(\sum_{j=1}^{3N}\left(\frac{\partial^2 E_{p(x_1,\dots x_{3N})}}{\partial x_j \partial x_i}\right)_0 x_j\right) \overset{\text{Schwartz}}{=} \sum_{i=1}^{3N}\sum_{j=1}^{3N}\left(\frac{\partial^2 E_p}{\partial x_i \partial x_j}\right)_0 x_i x_j$$

$$\Rightarrow E_p(x_1,\dots x_{3N}) = E_p(0,\dots 0) + \frac{1}{2}\sum_{i=1}^{3N} x_i \frac{\partial H}{\partial x_i}$$

$E_p(0) = E_p(0,\dots 0) = \text{const} = 0$ stavimo jer ne sadrži dinamiku kristalne rešetke

- naime za $x_i = 0$ $i = 1,\dots 3N$ sva energ. je sadrž. u E_K, tj. translac. energiji.

uprosječujemo preko Γ i kon. raspodjele

$$\Rightarrow \underline{\overline{E_p} = \frac{1}{2}\sum_{i=1}^{3N} x_i \overline{\frac{\partial H}{\partial x_i}} = \frac{3N}{2}kT}$$

($\overline{\frac{\partial H}{\partial x_i}} = kT$)

ta aprox. bolja za niže temp., što niže od tališta zbog viših članova

→ za Kartez. koordinate $E_K = \sum_{i=1}^{3N}\frac{m_i}{2}\dot{x}_i^2$ $\quad p_i = \frac{\partial E_K}{\partial \dot{x}_i} = m_i\dot{x}_i \Rightarrow E_K = \sum_{i=1}^{3N}\frac{p_i^2}{2m_i}$ $\quad \frac{\partial H}{\partial p_i} = \frac{\partial E_K}{\partial p_i} = \frac{p_i}{m_i}$ $\Rightarrow E_K = \frac{1}{2}\sum_{i=1}^{3N} p_i \frac{\partial H}{\partial p_i}$

$$\overline{E_K} = \frac{1}{2}\sum_{i=1}^{3N} p_i \overline{\frac{\partial H}{\partial p_i}} = \frac{3N}{2}kT$$

dopinos kin. energ.

→ **Ukupna energija kristalnog sistema** $H = E_K + E_p$ $\quad \bar{H} = \bar{E}_K + \bar{E}_p = \bar{U}$ mala fluktuacija što je veći broj čestica (atoma)

$$\underline{\bar{U} = \bar{E}_K + \bar{E}_p = 3NkT}$$

→ na temelju tog rezultata zaključujemo: 3N harm. oscilatora sa energ. kvantom kT

ta interpretacija nije potpuno dolazam

- ne možemo reći da je to skup nezavisnih harmoničkih oscilatora, ali može se pokazati da u kvadratičnoj aprox. (tako sistem realnih oscilatora (ograničimo se samo na kvadr. članove) se može zamijeniti na isti broj slobodnih oscilatora

⇒ dopinski kapacitet

$$C_V = \left(\frac{\partial \bar{U}}{\partial T}\right)_V = 3NX$$

1 mol $N = 6{,}03 \cdot 10^{23}$ $NX = R \approx 2$ cal/st.

$\Rightarrow C_{VM} = C_{V\,mola} = 3R \approx 6$ cal/st. Dulong - Petit (1819)

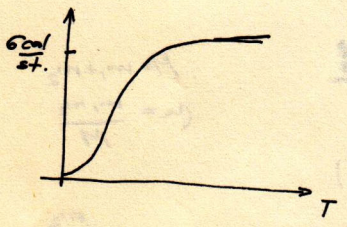
→ exp. podaci: Ag $C_V = A \cdot c_V$, $C_V = 0{,}055 \frac{cal}{st.}$ $\Rightarrow C_V = 5{,}94$ $T \approx 300$ K

	C_V
Li	5,16
Mg	6
Fe	6,1
Pb	6,4
Ag	5,94
To	6
C dijamant	1,4

na niskim temp. C_V mnogo manji tj. po III z.t-dm.

$\lim_{T \to 0} C_V = 0$

klas. statistička fizika stoji u proturječju s III z.t-dm.

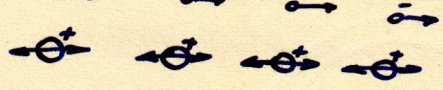


u klas. fizici nemoguće objasniti iščezavanje C_V na apsol. nul.

Debye $C_V \sim T^3$

→ dosljedno proturječje klas. teorije s eksperimentom

Metal N-atoma



→ elektroni koji su pobjegli iz dosega odgovarajućeg atoma djelovanja vanjske sile - slobodan el. plin

model koji dobro objašnjava el. i topl. vodljivost

topl. kapacitet ?

$C_{V\,met.} = C_{V\,ioni} + C_{V\,elektroni}$

$C_{V_i} = 3NX$ (suma energija tih harm. oscilatora)

pretp. 1 é po atomu $\Rightarrow C_{V_é} = \frac{3}{2}NX$ samo kin. energ. jer pretp. da je to slobodni el. plin

$\Rightarrow C_{V_m} = \frac{9}{2}NX \approx 9 \frac{cal}{st}$ mjerenja exp. daju kao i za izolatore 6 $\frac{cal}{st.}$

⇒ ne primjećuje se doprinos elektrona → zamrznuti stupnjevi slobode

nije uspjela objasniti klas. stat. fizika

→ primjena jednolike raspodjele energije

Idealan plin

- bez vanjskog polja

1) 1-A $\quad H = \sum_{i=1}^{N} \frac{p_{ix}^2 + p_{iy}^2 + p_{iz}^2}{2m}$

gdje $N = \tilde{N}$ broj mol. u jednom molu

po st. slob. $\frac{\chi T}{2}$ $\quad \bar{U} = \bar{H} = 3N\frac{\chi T}{2}$

ne ulazi ovolumenu stlačivost. za idealni plin

$$C_v = \left(\frac{\partial \bar{U}}{\partial T}\right)_V = \frac{3}{2}N\chi = \frac{3}{2}R$$

$$C_p - C_v = R \Rightarrow C_p = \frac{5}{2}R \Rightarrow \frac{C_p}{C_v} = \frac{5}{3}$$

dobro slaganje s eksperimentom $\quad C_v = 3\,\frac{cal}{st.}$ $\quad$ Ne, Ar, ... (sobna i visoke temp.)

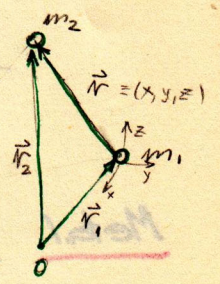
2) 2-A $\quad E_k = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2}$ $\quad m_1, m_2$ mase atoma

problem 2-tijela:

rel. koord. $\quad \vec{r} = \vec{r}_{12} = \vec{r}_2 - \vec{r}_1$ $\quad \vec{R} = \vec{r}_T = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{M}$ $\quad M = m_1 + m_2$, $\mu = \frac{m_1 m_2}{M}$

impuls težišta ili: $\quad \vec{P} = M\frac{d\vec{R}}{dt}$ $\quad \vec{P} \equiv (M\dot{X}_T, M\dot{Y}_T, M\dot{Z}_T)$

relat. impuls: $\quad \vec{p} \overset{def.}{=} \mu\frac{d\vec{r}}{dt}$ $\quad \vec{p} \equiv (\mu\dot{x}, \mu\dot{y}, \mu\dot{z})$



transl. energ.

$$\Rightarrow E_k = \frac{P^2}{2M} + \frac{p^2}{2\mu}$$

prosječne vrijednosti:

1. Kao za 1-A $\quad \frac{\overline{P^2}}{2M} = \frac{3}{2}\chi T$ $\quad$ jer $P^2 = \sum M\dot{X}^2$

2. U polarnom sustavu m_1 $\quad \vec{p} = \mu\vec{v}$

$$\vec{v} = \dot{r}\vec{r}_0 + r\dot{\vartheta}\vec{\vartheta}_0 + r\sin\vartheta\dot{\varphi}\vec{\varphi}_0 \Rightarrow p^2 = \mu^2(\dot{r}^2 + r^2\dot{\vartheta}^2 + r^2\sin^2\vartheta\dot{\varphi}^2)$$

$p_i = \frac{\partial L}{\partial \dot{x}_i}$ $\quad L = \overset{T-U}{E_k - E_p} = \frac{P^2}{2M} + \frac{p^2}{2\mu}$

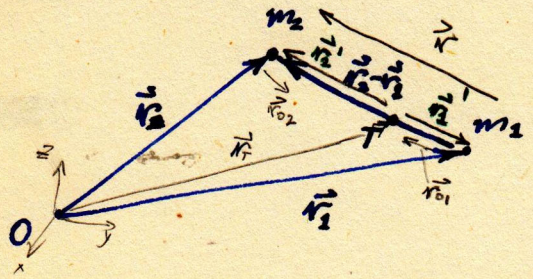
$$p_r = \frac{\partial L}{\partial \dot{r}} = \mu\frac{dr}{dt}$$

$$p_\vartheta = \frac{\partial L}{\partial \dot{\vartheta}} = \mu r^2\frac{d\vartheta}{dt}$$

$$p_\varphi = \frac{\partial L}{\partial \dot{\varphi}} = \mu r^2\sin^2\vartheta\frac{d\varphi}{dt}$$

$$\Rightarrow p^2 = p_r^2 + \frac{1}{r^2}\left(p_\vartheta^2 + \frac{1}{\sin^2\vartheta}p_\varphi^2\right)$$

Problem 2-dijela



$$\vec{F}_{jh} = -\operatorname{grad}_h U_{jh}(r_{jh})$$

$$\sum_{h=1}^{N}\sum_{j=1}^{N}\vec{F}_{jh}\,d\vec{r}_h = \frac{1}{2}\sum_{h=1}^{N}\sum_{j=1}^{N}\vec{F}_{jh}\,d\vec{r}_{jh} = -\frac{1}{2}\sum_{h=1}^{N}\sum_{j=1}^{N} dU_{jh}$$

$$= -\frac{1}{2}\,d\sum_{h=1}^{N}\sum_{j=1}^{N} U_{jh} = -dU_u \qquad \vec{F}_{hh}=0$$

$$\vec{r}_{12} = \vec{r}_2 - \vec{r}_1 \qquad \vec{R} = \vec{r}_T = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1+m_2}$$

$$\frac{d\vec{P}}{dt} = \sum_{h=1}^{N}\frac{d\vec{p}_h}{dt} = m\ddot{\vec{r}}_T = \sum_{h=1}^{N}\left(\vec{F}_h + \sum_{j=1}^{N}\vec{F}_{jh}\right) = \sum_{h=1}^{N}\vec{F}_h = \vec{F}$$

$$\vec{P} = \sum_{h=1}^{N}\vec{p}_h$$

$$\operatorname{grad} = \vec{r}_0\frac{\partial}{\partial r} + \vec{\vartheta}_0\frac{1}{r}\frac{\partial}{\partial\vartheta} + \vec{\varphi}_0\frac{1}{r\sin\vartheta}\frac{\partial}{\partial\varphi}$$

$$\frac{\partial}{\partial r}\vec{r}^{-1} = -1\,\vec{r}^{-2}$$

$$U_{12} = \frac{K_1 m_2}{r_{12}} = -\frac{G m_1 m_2}{r_{12}} \qquad K_1 = -Gm_1$$

$$\vec{F}_{12} = -\operatorname{grad}_2\frac{K_1 m_2}{r} = \frac{K_1 m_2}{r^2}\vec{r}_{02}$$

na masu tocku 2 djeluje 1 usmjerena

$$U_{21} = \frac{K_2 m_1}{r_{21}} = -\frac{G m_1 m_2}{r_{21}} \qquad K_2 = -Gm_2$$

$$\vec{F}_{21} = -\operatorname{grad}_1\frac{K_2 m_1}{r} = \frac{K_2 m_1}{r^2}\vec{r}_{01}$$

$$|\vec{r}_{12}| = |\vec{r}_{21}| \qquad \vec{r}_{01} = -\vec{r}_{02}$$

$$U_{hh}=0$$

$$U_u = \frac{1}{2}\sum_{h=1}^{2}\sum_{j=1}^{2}U_{jh} = \frac{1}{2}(U_{12}+U_{21}) = \frac{m_1 m_2}{r} = \frac{K_1 m_2}{r_{12}}$$

$$\Rightarrow \vec{F}_{12} = -\vec{F}_{21}$$

$$\vec{r}_{12} = \vec{r} = \vec{r}_2' - \vec{r}_1' \qquad \& \qquad \vec{r}_T' \quad 0 = m_1\vec{r}_1' + m_2\vec{r}_2'$$

$$0 = m_1\dot{\vec{r}}_1' + m_2\dot{\vec{r}}_2'$$

$$\dot{\vec{r}} = \dot{\vec{r}}_2' - \dot{\vec{r}}_1'$$

$$\dot{\vec{r}}_2' = -\frac{m_1}{m_2}\dot{\vec{r}}_1'$$

$$\dot{\vec{r}} = \left(-\frac{m_1}{m_2} - 1\right)\dot{\vec{r}}_1'$$

$$\dot{\vec{r}}_1' = -\frac{m_2}{m_1+m_2}\dot{\vec{r}}$$

$$\dot{\vec{r}}_2' = \frac{m_1}{m_1+m_2}\dot{\vec{r}}$$

$$E_K = \frac{1}{2}\left[\frac{p_1^2}{m_1} + \frac{p_2^2}{m_2}\right]$$

$$\vec{p}_1 = m_1\dot{\vec{r}}_1 \qquad \vec{p}_2 = m_2\dot{\vec{r}}_2$$

$$\vec{r}_1 = \vec{r}_T + \vec{r}_1' \qquad \vec{r}_2 = \vec{r}_T + \vec{r}_2'$$

$$\vec{p}_1 = m_1\dot{\vec{r}}_T + m_1\dot{\vec{r}}_1' \qquad \vec{p}_2 = m_2\dot{\vec{r}}_T + m_2\dot{\vec{r}}_2'$$

$$E_K = \frac{1}{2}\left[m_1(\dot{\vec{r}}_T + \dot{\vec{r}}_1')^2 + m_2(\dot{\vec{r}}_T + \dot{\vec{r}}_2')^2\right]$$

$$= \frac{1}{2}\left[(m_1+m_2)\dot{\vec{r}}_T^{\,2} + \dot{\vec{r}}_T(\underbrace{m_1\dot{\vec{r}}_1' + m_2\dot{\vec{r}}_2'}_{!!\ 0}) + m_1\dot{\vec{r}}_1'^{\,2} + m_2\dot{\vec{r}}_2'^{\,2}\right]$$

$$E_K = \frac{\vec{p}^{\,2}}{2M} + \frac{1}{2}\left[m_1\dot{\vec{r}}_1'^{\,2} + m_2\dot{\vec{r}}_2'^{\,2}\right]$$

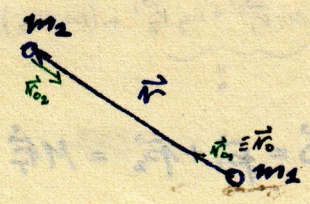
$$\left[\frac{+m_1m_2^2 + m_2m_1^2}{(m_1+m_2)^2}\right]\dot{\vec{r}}^{\,2} = \frac{m_1m_2(m_1+m_2)}{(m_1+m_2)^2}$$

$$E_K = \frac{p^2}{2M} + \frac{1}{2}\mu\,\dot{\vec{r}}^{\,2} \qquad \mu = \frac{m_1m_2}{M}$$

$$\underbrace{m_1\dot{\vec{r}}_1' + m_2\dot{\vec{r}}_2'}_{!!\ 0} + (m_1+m_2)\dot{\vec{r}}_T$$

$$\vec{P} = \vec{p}_1 + \vec{p}_2 = M\dot{\vec{r}}_T = M\frac{d\vec{R}}{dt}$$

$$M = m_1 + m_2$$



$$U_{12} = \frac{kr^2}{2} = U_{21}$$

$$\vec{F}_{12} = -\text{grad}_2 \frac{kr^2}{2} = -kr \cdot \vec{r}_{02}$$

na mjestu 2. ali 1. u sustavu

$$\vec{F}_{21} = -\text{grad}_1 \frac{kr^2}{2} = -kr \cdot \vec{r}_{01}$$

$$\vec{F}_{12} = -\vec{F}_{21}$$

$$U_u = \frac{1}{2}(U_{12} + U_{21}) = \frac{k}{2} r^2$$

$$\vec{F}_{12} = m_2 \ddot{\vec{r}}_2 = m_2 (\ddot{\vec{r}} + \ddot{\vec{r}}_1') = m_2 \ddot{\vec{r}} + \frac{m_2}{m_1} (m_1 \ddot{\vec{r}}_1') \quad (\vec{F}_{21} = -\vec{F}_{12}) \Rightarrow \vec{F}_{12} = \frac{m_1 m_2}{m_1 + m_2} \ddot{\vec{r}}$$

dobijemo na 2 načina

ili transf. u dva sustava: Kaže da ta sila djeluje iz sustava koji miruje (centra mase)

$$\left.\begin{aligned} m_2 \ddot{\vec{r}} &= \vec{F}_{12} + (-m_2 \ddot{\vec{r}}_1') \\ \ddot{\vec{r}}_1' &= -\frac{m_2}{m_1 + m_2} \ddot{\vec{r}} \end{aligned}\right\} \Rightarrow \vec{F}_{12} = \frac{m_2 m_1 + m_2^2 - m_2^2}{m_1 + m_2} \ddot{\vec{r}}$$

$m \vec{a}(S,t) = m \vec{a}'(S',t) + m \vec{a}_0(S,t)$ + 0 ako nema rotacije

gibanje S' u S

S - sustav mase

S' - sustav T

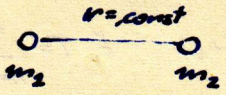
$$\mu \ddot{\vec{r}}_1 = \vec{F}_{12} = -kr \cdot \vec{r}_0 \Rightarrow \mu \ddot{r} + kr = 0$$

$\ddot{\vec{r}} \cdot \vec{r}_0$ za lin. g.h.

$$\Rightarrow \omega^2 = \frac{k}{\mu}$$

$$\Rightarrow U_u = \frac{\mu \omega^2 r^2}{2}$$

→ slika koju stvorimo mora biti zasnovana na exp.
exp. pokazuje $r = \text{const.}$ dobrom gibanja



$\Rightarrow p_r = 0$

ostaju p_ϑ, p_φ → 2 st. slobode

$p^2 = \frac{1}{r^2}\left(p_\vartheta^2 + \frac{1}{\sin^2\vartheta} p_\varphi^2\right)$ & primjena zak. jednake raspodj. energ.

$$\overline{\frac{p^2}{2\mu}} = 2 \cdot \frac{\chi T}{2} = \chi T$$ ⇒ sr. vrij. rotac. < sr. vrij. translac.

$$\Rightarrow \underline{\bar{E}_k = \frac{5}{2}\chi T}$$

→ za 1 mol $N = \tilde{N}$ ⇒ $\bar{U} = \frac{5}{2}\tilde{N}\chi T$ $C_v = \left(\frac{\partial \bar{U}}{\partial T}\right)_V$

$$\underline{C_v = \frac{5}{2}R} \quad C_p = \frac{7}{2}R \quad \underline{\frac{C_p}{C_v} = \frac{7}{5}}$$

Primjer: H_2

exp. ⇒ ispod 80°K $C_v \to \frac{3}{2}R$ → zamrzavanje rotac. st. slobode

za druge molek. tek ispod 10°K

→ iznad sobne temp. $T \gtrsim 5000$K r - nije const.

pogrešno bi bilo uzeti $\frac{3}{2}KT$ umjesto $2\cdot\frac{KT}{2}$

za dovoljno male oscilacije duž r - harm. oscilator
→ potrebno uzeti pod. energ. oscil.

$$E_{osc} = \frac{p_r^2}{2\mu} + \frac{\mu\omega^2 r^2}{2}$$ budući $\mu\ddot{\vec{r}} = \vec{F}_{12} = -kr\vec{r}_0 \Rightarrow \omega^2 = \frac{k}{\mu}$

$U_u^{osc} = \frac{k}{2}r^2 = \frac{\mu\omega^2 r^2}{2}$

? →

$$\bar{E}_{osc.} = 2\cdot\frac{\chi T}{2} = \chi T$$

$$\Rightarrow \underline{\bar{U} = \tilde{N}\left(\frac{3}{2}\chi T + \chi T + \chi T\right) = \frac{7}{2}\tilde{N}\chi T}$$
(transl. rot. oscil.)

dalje kanonska raspodjela $\frac{9}{2}R$

$$\underline{C_v = \frac{7}{2}R} \quad C_p = \frac{9}{2}R \quad \frac{C_p}{C_v} = \frac{9}{7}$$

za dovoljno vis. temp.

3) Više - A

$2T = m v_T^2 + \sum_{i=1}^{3} I_i \omega_i^2$ za sustav gl. osi. ($\vec{0} \equiv T$ & $J_{pq} = 0$)

$H = T + U$ $\quad E_k\, T = \sum_{h=1}^{N} \left[\frac{1}{2} m_h S \dot{x}_{h_T}^2 + \frac{1}{2} S I_{gh} \omega_{gh}^2 + \sum_{k=1}^{Sas} \frac{1}{2} m_{hk} \dot{x}_{hk}^2 \right]$

$E_p = U = \sum_{h=1}^{N} \left[\sum_{k=1}^{Sas} \frac{4\pi^2 m_{hk} \nu_{hk} x_{hk}^2}{2} \right]$ — sano 3 harm. oscil. / a nama vanj. polja niti interakcija

Kao krutо tijelo

$\Rightarrow \overline{E_{k\,transl.\,tež.\,h\text{-}molek.}} = \frac{3}{2} \chi T$

$E_{h\,rot} = \frac{1}{2} \sum_{i=1}^{3} I_i \omega_i^2$

$= \frac{1}{2} \sum_{i=1}^{3} \frac{M_i^2}{I_i}$

za sustav glavnih osi ($\vec{0} \equiv T$ & slob. os. $J_{pq} = 0$)

Označimo $\vec{M} = \vec{\Gamma}_T^2$ moment impulsa krutog tijela u sustavu gl. osi. tj. u odnosu na T

$\Rightarrow M_i = \Gamma_{i_T}^1 = I_i \omega_i$

tenzor inerc. u sustavu gl. osi.:

$$J = \begin{pmatrix} I_1 & 0 & 0 \\ 0 & I_2 & 0 \\ 0 & 0 & I_3 \end{pmatrix} \qquad \vec{M} = J \cdot \vec{\omega}$$

formalno: $m \ldots J$, $p \ldots M$

→ ako ω_i shvatimo kao gen. koord. ili M_i kao gen. impulse & primj. zakon jednako raspodjele

$\overline{E_{h\,rot}} = \frac{3}{2} \chi T$

→ za mol. $N = \tilde{N}$ $\Rightarrow \bar{U} = 3 \tilde{N} \chi T$ $\Rightarrow$ $C_v = 3R$ $C_p = 4R$ $\frac{C_p}{C_v} = \frac{4}{3}$

→ najviša temp. dolazi do oscilacija - udalj. atoma prostaju biti konst.

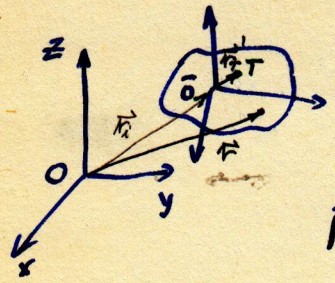
n-atoma u molekuli $\Rightarrow$ $3n$ - ukupan broj st. slobode u molek.

3 transl	$3 \cdot \frac{\chi T}{2}$	ukl. energ 1 mol. $(3n-3)\chi T$
3 rotac.	$3 \cdot \frac{\chi T}{2}$	
$(3n-6)$ oscil. st. slob. harmon. oscilatora	$(3n-6)\chi T$	

Cijeloj plina (1 mol.)

$\bar{U} = \tilde{N}(3n-3)\chi T = (3n-3)RT$

$\Rightarrow C_v = 3(n-1)R$ $\quad C_p = (3n-2)R$ $\quad \frac{C_p}{C_v} = \frac{3n-2}{3n-3}$ $\quad$ bidno!!! $n > 2$



$$\vec{\Gamma} \overset{def}{=} \int_V \vec{r} \times \dot{\vec{r}}\, dm$$

moment impulsa u odnosu na Oxyz

$$\vec{\Gamma} = m\vec{r}_T \times \vec{V}_{\bar{O}} + m\vec{r}_{\bar{O}} \times (\vec{\omega} \times \vec{r}_T') + \underbrace{\int_V \vec{r}' \times (\vec{\omega} \times \vec{r}')\, dm}_{\vec{\Gamma}'}$$

$\vec{\Gamma}'$ sobzirom na slobodište $\bar{O}$

za $\bar{O} \equiv T$ $\quad \vec{r}_T' = 0$ $\quad \vec{\Gamma} = m\vec{r}_T \times \vec{V}_T + \vec{\Gamma}_T'$ sobzirom na T

općenito: $\vec{\Gamma}' = \sum \vec{r}' \vec{\Gamma}' = J \cdot \vec{\omega}$

$$\begin{pmatrix} \Gamma_\xi' \\ \Gamma_\eta' \\ \Gamma_\zeta' \end{pmatrix} = \begin{pmatrix} I_\xi & -D_{\xi\eta} & -D_{\xi\zeta} \\ -D_{\eta\xi} & I_\eta & -D_{\eta\zeta} \\ -D_{\zeta\xi} & -D_{\zeta\eta} & I_\zeta \end{pmatrix} \begin{pmatrix} \omega_\xi \\ \omega_\eta \\ \omega_\zeta \end{pmatrix}$$

za $\bar{O} \equiv T$ & slob. osi: $\vec{\Gamma}_T' = J \cdot \vec{\omega}$

$$\vec{\Gamma}_T' = \vec{\Gamma}_T^{\perp} = \sum_{i=1}^{3} I_i \omega_i \vec{\omega}_{oi}$$

$$\begin{pmatrix} \Gamma_{1T}^{\perp} \\ \Gamma_{2T}^{\perp} \\ \Gamma_{3T}^{\perp} \end{pmatrix} = \begin{pmatrix} I_1 & 0 & 0 \\ 0 & I_2 & 0 \\ 0 & 0 & I_3 \end{pmatrix} \cdot \begin{pmatrix} \omega_1 \\ \omega_2 \\ \omega_3 \end{pmatrix}$$

gdje $\vec{\omega}_{oi}$ slobodne osi tenzora inercije

spec. slučaj : atomi na pravcu - n-atoma

položaj sustava

sa ϑ, φ odredan položaj molek.

2 rot. st. slobode

3 transl.	$\frac{3}{2}\chi T$	1 molplina
2 rot	χT	
$(3n-5)$ oscil.	$(3n-5)\cdot\chi T$	

1 rot. st. prešao na oscil.

$$\bar{U} = \tilde{N}\left(3n-\frac{5}{2}\right)\chi T = \left(3n-\frac{5}{2}\right)RT$$

$$C_V = \left(3n-\frac{5}{2}\right)R \qquad C_p = \left(3n-\frac{3}{2}\right)R \qquad \frac{C_p}{C_V} = \frac{6n-3}{6n-5}$$

Plin u gravitacionom polju

postup : izjeli sistem na **istoj** temp. T i t-din. ravnoteža (uvjet za izvod Kan. raspodjele)

→ aprox. za atmosferu !

& **idealan plin** (nema interakcije) *) Bucol. stroza (Mlić') gdje $dW' = \frac{e^{-\frac{u(x,y,z)}{\chi T}}\,dx\,dy\,dz}{\iiint e^{-\frac{(x,y,z)}{\chi T}}\,dx\,dy\,dz}$

Kan. raspodj. => **gustoća Kan. ansambla**

$$\varrho \sim e^{-\frac{E}{\chi T}}$$

$$\bar{E}_p(x) = mgx \qquad \varrho(x) = \varrho(0)\, e^{-\frac{mgx}{\chi T}}$$

broj čest. $\quad N(x) = N(0)\, e^{-\frac{mgx}{\chi T}}$

$$\Rightarrow \frac{N(x_2)}{N(x_1)} = e^{\frac{mg(x_1-x_2)}{\chi T}}$$

za idealni plin (zbog *) $\quad PV = N\chi T \quad \Rightarrow P \sim N \qquad V = 1\ cm^3$

$$P(x) = P(0)\, e^{-\frac{mgx}{\chi T}} \qquad \frac{P(x_2)}{P(x_1)} = e^{\frac{mg(x_1-x_2)}{\chi T}}$$

u sloju $x_1 - x_2$ temp. **ista**

Perrin : odred. χ $\quad \ln\frac{N(x_2)}{N(x_1)} = mg\,\frac{x_1-x_2}{\chi T}$

uzeo koloidne čestice mase $\approx 10^{-4}$ gm
gustoće malo veće od vode - lebde

Znamo Kons. - brojem čestica

→ Do sada smo zanemarivali doprinos gravitac. polja na topl. kapacitet plina!

Kolika je sr. energ. plina u gravitac. polju

→ **račun parcio. ffje** $z_p \rightarrow f_p = -kT \ln z_p$

$$H = T + U = \sum_{h=1}^{N} \left\{ \left[\frac{1}{2} m_h S \dot{x}_h^2 + SS' a_{q_h q_h}(\varphi_h, \vartheta_h) \dot{\varphi}_h \dot{\vartheta}_h + \sum_{\kappa=1}^{S_{ose}} \frac{1}{2} m_{h\kappa} \dot{x}_{h\kappa}^2 \right] + \left[U_{vh}(x_h, y_h, z_h, \varphi_h, \vartheta_h) + \sum_{\kappa=1}^{S_{ose}} \frac{4\pi^2 m_{h\kappa} \nu_{h\kappa} x_{h\kappa}^2}{2} + U_{int}(x_i, y_i, z_i, \varphi_i, \vartheta_i) \right] \right\}_{i=1,\dots N}$$

1-A idealni plin u gravitac. polju $\vec{g} = -g\vec{\imath}$ $\quad \vec{F} = -\mathrm{grad}(mgx)$

$$\Rightarrow H = \sum_{h=1}^{N} \left[\frac{1}{2} m_h S \dot{x}_h^2 + m_h g x_h \right]$$

bez interakcije: pot. energ. oscil.

općenito: $H = H(\dot{x}_1, \dots \dot{x}_S, x_{11}, \dots x_{NS_{os}}) + \sum_{h=1}^{N} U_{vh}(x_h, y_h, z_h)$ $\quad S' = 6 \cdot N$

$$dW = A e^{-\frac{H}{kT}} d\phi \qquad Z = A \int_{\Gamma} e^{-\frac{H}{kT}} d\phi \qquad A = \frac{1}{N! h^{S'}}$$

$$Z = A \int_{\Gamma} e^{-\frac{1}{kT}\left[H(\dot{x}_1, \dots \dot{x}_S, x_1, \dots x_{NS_{os}}) + \sum_{h=1}^{N} U_{vh}(x_h, y_h, z_h) \right]} d\phi$$

$$Z = \underbrace{\frac{A}{a^{N}} \int_{\Gamma'} e^{-\frac{1}{kT}\left[H(\dot{x}_1, \dots \dot{x}_S, x_1, \dots x_{NS_{os}}) \right]} d\phi'}_{Z'} \cdot \underbrace{a^N \prod_{h=1}^{N} \int_{x_{h\min}}^{x_{h\max}} \int_{y_{h\min}}^{y_{h\max}} \int_{z_{h\min}}^{z_{h\max}} e^{-\frac{U_{vh}(x_h, y_h, z_h)}{kT}} dx_h\, dy_h\, dz_h}_{Z_p^N}$$

$$U_{vh} = mgx_h \quad \Rightarrow \quad Z_p = a \int_{x_{min}}^{x_{max}} e^{-\frac{mgx}{kT}} dx$$

particl. fja pot. energ. za 1 molek.

$$Z_{pot} = a \int_{0}^{l} e^{-\frac{mgx}{kT}} dx = \frac{akT}{mg}\left(1 - e^{-\frac{mgl}{kT}}\right)$$

l - visina stupca plina

$$F = -kT \ln Z = \underbrace{-kT \ln Z'}_{F'} \underbrace{- NkT \ln z_p}_{N \cdot f_p} \qquad \beta = \frac{1}{kT}$$

$$f_p = -kT \ln z_p$$

$$\bar{U} = -\left(\frac{\partial}{\partial \beta} \ln Z\right)_{V,a'} = -\left(\frac{\partial \beta F}{\partial \beta}\right)_{V,a'} = \left(\frac{\partial}{\partial \beta} \ln Z'\right)_{V,a'} \underbrace{-N\left(\frac{\partial}{\partial \beta} \ln z_p\right)}_{N \cdot \bar{E}_p}$$

jer $\ln Z = \ln Z' + N \ln z_p$

srednja pot. energ. jn 1 molek.

$$\bar{E}_p = -\frac{d}{d\beta}(\ln z_p)_V \overset{f_p = -kT \ln z_p}{=} \frac{d}{d\beta}(\beta f_p)_V$$

$$S' = -\left(\frac{\partial F}{\partial T}\right)_{V,a'} \quad ;\!; \quad F = U - TS \quad \Rightarrow \quad F' + N f_p = -\left(\frac{\partial}{\partial \beta} \ln Z'\right)_{V,a'} + N\bar{E}_p - TS' - TNs_p$$

$$\Rightarrow f_p = \bar{E}_p - Ts_p \quad \Rightarrow \quad s_p = \frac{\bar{E}_p - f_p}{T}$$

entropija uodnosu na pot. energ. 1 molek.

$$S = \underbrace{-\left(\frac{\partial F}{\partial T}\right)_{V,a'}}_{S'} \underbrace{- N\left(\frac{\partial f_p}{\partial T}\right)_{V,a'}}_{N \cdot s_p} \quad \Rightarrow \quad s_p = -\left(\frac{\partial f_p}{\partial T}\right)_{V,a'}$$

3.5.3. Maxwell-Boltzmann-ova formula u prisustvu vanjskih sila

Maxw.-Boltz. $dW = \dfrac{e^{-\frac{\mathcal{H}_h(\xi_1,\dots p_s,b)}{\chi T}}\, d\xi_1 \dots dp_s}{\int_{(\omega_h)} e^{-\frac{\mathcal{H}_h(\xi_1,\dots p_s,b)}{\chi T}}\, d\xi_1 \dots dp_s}$ $\quad b=\{\xi_1,\dots\xi_s$ skup stab. ind. sa $(N-1)\}$ $\quad s \le sN$

$\mathcal{H}_h(\xi_1,\dots p_s,b) = \mathcal{H}_h(\xi_{h_1},\dots p_{hs},b) = \underbrace{\mathcal{H}_{0h}(\xi_{h_1},\dots p_{hs})}_{T_h^{tot}(\xi_{h_1},\dots p_{hs}) + U_h^{int}(\xi_1,\dots\xi_{hs})} + \mathcal{H}_{int_h}(\xi_1,\dots\xi_s)$

s-st. slob. molek. — akcena translac. gen. koord. — ako polaznji atoma pri DOT & OSC. ne utjecu na ukupnu pot. energ. molekule — ovisi samo o polozaju centra mase — takva invarijanca

$$\mathcal{H}(\xi_1,\dots p_s,b) = T_h^{tot}(p_1,\dots p_s) + U(x_h,y_h,z_h) + \mathcal{H}_{int_h}(x,y,z,\xi_1,\dots\xi_{3(N-1)})$$

$(p_x,p_y,p_z,\dots) + U_h^{osc.}(x_{h_1},\dots x_{hN})$

ili $\quad \mathcal{H}(\xi) = U(x,y,z) + \mathcal{H}^*(\xi^*)$

$\xi^* = \{$ Komp. impulsa, koordinate unutrasnjih kvadanja u molekuli, koordinate koje odredjuju molek. interakciju $\}$

(x,y,z) koord. centra mase

općenito: $\xi^* = \{\xi^{*\prime}, x,y,z\} = \{x,y,z, \underbrace{p_1,\dots p_s, x_{h_1},\dots x_{hN}}_{\xi^{*\prime}}, \xi_1,\dots\xi_{3N-3}\}$ $\quad \& \xi_1,\dots\xi_{3N-3}$

*) → ako je polje idealno tada u $\mathcal{H}^*$ nema koordinata x,y,z

$$dW' = \int_{(\omega_{(x,y,z)})} dW = \frac{e^{-\frac{U(x,y,z)}{\chi T}}\, dx\,dy\,dz \int e^{-\frac{\mathcal{H}^*(\xi^{*\prime},x,y,z,\xi_1,\dots\xi_{3N-3})}{\chi T}} \cdot d\xi^{*\prime}}{\iiint e^{-\frac{U(x,y,z)}{\chi T}} \left(\int e^{-\frac{\mathcal{H}^*(x,y,z,\xi^{*\prime})}{\chi T}} d\xi^{*\prime} \right) dx\,dy\,dz}$$

*) $\Rightarrow$ $$dW' = \frac{e^{-\frac{U(x,y,z)}{\chi T}}\, dx\,dy\,dz}{\iiint e^{-\frac{U(x,y,z)}{\chi T}}\, dx\,dy\,dz}$$

→ vjerojatnost da se molekula idealnog plina nalazi u volumenu $dx\,dy\,dz$ u okolini točke (x,y,z)

$dn = N\,dW'$ $\quad N$ - broj molek. u V $\Rightarrow \dfrac{dn}{dV} = \dfrac{N e^{-\frac{U(x,y,z)}{\chi T}}}{\iiint e^{-\frac{U(x,y,z)}{\chi T}}\, dx\,dy\,dz} \Rightarrow$ $\boxed{n_0 = \dfrac{N}{\iiint e^{-\frac{U(x,y,z)}{\chi T}}\, dx\,dy\,dz} > \dfrac{N}{V}}$ ← srednja gustoća

n_0 - broj molek. u $1\,cm^3$ na mjestu (x_0,y_0,z_0)

$U(x_0,y_0,z_0) = 0$

$$dn = n_0\, e^{-\frac{U(x,y,z)}{\chi T}}\, dx\,dy\,dz$$

broj molek. po jedinici volumena $\quad n = \dfrac{dn}{dV} = n_0\, e^{-\frac{U(x,y,z)}{\chi T}}$

$$f_p = -\chi T\left[\ln\frac{a\chi T}{mg} + \ln\left(1 - e^{-\frac{mgl}{\chi T}}\right)\right]$$

→ stlpac plina velik ili malen

1) $mgl \gg \chi T$ plin u atmosferi

$$f_p \approx -\chi T \ln\frac{a\chi T}{mg}$$

$$\bar{E}_p = \frac{d}{d\beta}(\beta f_p)_{V,a'} = \frac{d}{d\beta}\left(-\ln\frac{a}{\beta mg}\right) = -\frac{\beta mg}{a}\cdot\frac{a}{mg}\left(-\frac{1}{\beta^2}\right) = +\frac{1}{\beta}$$

$$S_p = \frac{\bar{E}_p - f_p}{T}$$

$$\Rightarrow \bar{E}_p = \chi T \qquad S_p = \chi\left(\ln\frac{a\chi T}{mg} + 1\right)$$

$$\frac{d\bar{E}_p}{dT} = \chi \qquad C_v = \left(\frac{\partial \bar{U}}{\partial T}\right)_V \qquad \bar{U} = -\left(\frac{\partial}{\partial\beta}\ln Z'\right)_{V,a'} + N\bar{E}_p$$

za 1 mol $N = \tilde{N}$ doprinos C_v je $\tilde{N}k = R = \frac{2a'}{st}$ → reda velič. kao doprinos Kin. energ. molek

⇒ uzeti u obzir

2) $mgl \ll \chi T$ $\qquad e^{-\frac{mgl}{\chi T}} = 1 - \frac{mgl}{\chi T} + \frac{1}{2}\left(\frac{mgl}{\chi T}\right)^2 + \dots$

$$\Rightarrow \ln\left(1 - e^{-\frac{mgl}{\chi T}}\right) \approx \ln\left[\frac{mgl}{\chi T}\left(1 - \frac{mgl}{2\chi T}\right)\right] =$$

$$\ln(1-x) = -\left[x + \frac{x^2}{2} + \frac{x^3}{3} + \frac{x^4}{4} + \dots\right] \quad -1 \le x < 1 \qquad x = \frac{mgl}{2\chi T} \ll 1$$

$$\approx -x \quad \text{za} \quad x \ll 1$$

$$= \ln\left(\frac{mgl}{\chi T}\right) - \frac{mgl}{2\chi T}$$

$$\Rightarrow f_p = -\chi T\left[\ln\frac{a\chi T}{mg}\cdot\frac{mgl}{\chi T} - \frac{mgl}{2\chi T}\right] = \underbrace{-\chi T\ln al}_{-\frac{1}{\beta}\ln al} + \frac{mgl}{2}$$

$$\bar{E}_p = \frac{d}{d\beta}(\beta f_p)_{V,a'} = \frac{d}{d\beta}\left(-\ln al + \beta\frac{mgl}{2}\right)_{V,a'} = \frac{mgl}{2}$$

$$S_p = \frac{\bar{E}_p - f_p}{T} = \frac{\chi T\ln al}{T} = \chi\ln al \qquad = -\left(\frac{\partial f_p}{\partial T}\right)_{V,a'} \quad V = f(l)$$

⇒ nepotrebna korekcija

→ laboratorijski uvjeti: $m = 10^{-24}g$, $l = 1m$ $\Rightarrow mgl \approx 10^{-24+8+2} = 10^{-19}$ erg

$$\chi T \approx 10^{-16}\frac{erg}{st}\cdot 10^{-3}K = 10^{-19}erg \qquad \text{za } T = 10^{-3}K$$

praktički na svim T $\quad mgl \ll \chi T$

Rezime

Primjena idealne raspodj. energije: 1. lokalni plin
2. Titranje kristala
3. Zrač. crnog tijela

Zračenje crnog tijela

$$U = aVT^4 \qquad \text{Stefan-Boltzmann}$$

→ energija el.magn. valova u posudi

→ izvod Supek I (III izdanje) 426. str. - ovdje plauzibilno objašnjeno

9. Ekvivalentnost harm. oscilatora i ravnog vala

& Mušicki II 191. str.

$$\vec{E} = -\frac{1}{c}\dot{\vec{A}}$$

$$\vec{H} = \operatorname{rot}\vec{A} \qquad \operatorname{div}\vec{A} = 0$$

$$\vec{A} = \sum_{\vec{\Omega}} \vec{A}_{\Omega}\, e^{i\vec{\Omega}\cdot\vec{r}} \qquad \Omega = \frac{2\pi}{\lambda} \quad \text{valni vektor}$$

iz val. jbe za $\vec{E}$ & $\vec{H}$ ⇒ vrem. ovisnost A_{Ω}

$$\ddot{A}_{\Omega} = -\omega^2(\Omega) A_{\Omega}$$

Hamiltonijan $\quad H = \sum_{\Omega} H_{\Omega} \qquad H_{\Omega} = \frac{1}{2}\left[P_{\Omega}^2 + \omega^2(\Omega) Q_{\Omega}^2\right]$

⇒ $\bar{E}(\Omega) = \bar{H}_{\Omega} = KT$ jer harm. oscilator

→ ukupna energija el.magn. vala = $\sum$ energ. harm. oscilatora (svih)

titranje harmon. oscilatora i po modelu prema kojem smo poslali trodimenzionalni titranje kristala

frekvencija el.m. valova:

$0 < \omega(\Omega) < \infty \qquad \omega = 2\pi\nu = 2\pi\frac{c}{\lambda} = c\cdot\Omega$

$\forall\Omega$ karakterizira 1 harm. oscilator

→ energija el.m. valova (zračenja)

$$U = 2\sum_{\vec{\Omega}} \bar{E}(\Omega)$$

→ srednja vrij. jer se P_{Ω} & Q_{Ω} mijenjaju u vremenu

→ kod el.m. vala isti Ω imaju 2 titranja (vala) sumirano preko polarizacije

Mušicki II 194.

$$U = \frac{1}{2}\sum_{\vec{k},\sigma}\left[\left(P_k^{\sigma}\right)^2 + \omega_k^2\left(Q_k^{\sigma}\right)^2\right]$$

→ nije osobito važno kolike su dim. posude u kojoj se nalaze el.m. valov. o njima ne ovisi fiz. situacija

→ periodično ponavljanje svojstava, što karakterizira el.m. valove pomakom za L lijevo ili desno ne dobiv. ništa novo

→ Kocka $V = L^3$ za koju imamo period. ponavljanje

→ R.U. (rubni uvjeti)

$$\vec{A} = \sum_{\vec{q}} \vec{A}_q e^{i\vec{q}\vec{r}} \Rightarrow e^{iq_x \cdot x} = e^{iq_x (x+L)}$$

$$\Rightarrow q_x \cdot L = 2\pi n_x$$

$$q_x = \frac{2\pi}{L} \cdot n_x \qquad n_x, n_y, n_z = 0, \pm 1, \pm 2, \ldots$$

$$q_y = \frac{2\pi}{L} \cdot n_y$$

$$q_z = \frac{2\pi}{L} \cdot n_z$$

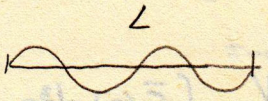
→ Komponente valnog vektora kao kvantizirane veličine a za nj. smo ispoč. pretpostavili da je kontinuirana veličina, ali zamislimo $L \to \infty$ ⇒ Fourier. Σ → Four. integral

1-D.im. slučaj

$$q = \frac{2\pi}{L} \cdot n = \frac{2\pi}{\lambda} \qquad L = n \cdot \lambda$$

→ periodički rubni uvjeti izražavaju zahtjev da na dužini perioda L ima cijeli broj valnih duzina

Kvantiziran q → kvantiz. λ



što manje značenje kvantizacije što je duzina L veća

Svrha toga: prijelazom na diskontinuum možemo prebrojiti konačna stanja pa zatim prijeći na kontinuum

→ Koliko različitih stanja ima u infinit. intervalu (volumenu) d^3q

$$d^3\vec{q} = dq_x\, dq_y\, dq_z = \left(\frac{2\pi}{L}\right)^3 dn_x dn_y dn_z = \left(\frac{2\pi}{L}\right)^3 d^3n$$

$$d^3n = dn_x dn_y dn_z = \left(\frac{L}{2\pi}\right)^3 d^3\vec{q} \qquad = \frac{L^3}{(2\pi)^3} d^3\vec{q}$$

možemo sa sume prijeći na integral

$$\sum_{\vec{q}} F(\vec{q}) \;\to\; \int F(\vec{q})\, d^3n = \frac{V}{(2\pi)^3} \int F(\vec{q})\, d^3\vec{q} \qquad L^3 = V$$

$= \sum_i F(\vec{q}_i) \cdot n_i$

→ odranije opći recept za prijelaz od $\Sigma \to \int$

$$\sum_i \vec{q}_i \;\to\; \int \frac{d\phi}{h^3}$$

$\vec{q}_i$: ukupni broj stanja u faznom prostoru; 1: višestrukost stanja i-te energije E_i; h^3: br. st. slobode; vodi primjenom na

→ promatramo stanja različitih energija - karakterizirano sa različ. $\vec{q}$

$$\int_V d\phi = \int_V dx\, dy\, dz\, dp_x\, dp_y\, dp_z \;\to\; V d^3p$$

jer cijelo zračenje zatvoreno u posudi volum. V pa možemo odmah integrirati

De Broglie $\qquad p = \frac{h}{\lambda} = \frac{h}{2\pi} \cdot \frac{2\pi}{\lambda} = \frac{h}{2\pi} \cdot \vec{q}$

$$d^3p = \left(\frac{h}{2\pi}\right)^3 d^3\vec{q}$$

$$\int \frac{d\phi}{h^3} = \frac{\int d^3\vec{r} \cdot \int d^3p}{h^3} = \frac{V}{h^3} \cdot \left(\frac{h}{2\pi}\right)^3 \int d^3\vec{q} = \frac{V}{(2\pi)^3} \int d^3\vec{q}$$

$n_{x_h} = n_{3h-2}$, $\vec{q}(n)_x$

$$\to\; U = 2 \sum_{\vec{q}} \bar{E}(\vec{q}) = 2 \cdot \sum_i E(\vec{q}_i)\, n_i \;\to\; 2 \int \bar{E}(\vec{q})\, d^3n = 2 \cdot \frac{V}{(2\pi)^3} \int \bar{E}(\vec{q})\, d^3\vec{q}$$

$2\pi\nu = 2\pi \frac{c}{\lambda}$ $\qquad \omega_x, \omega_y, \omega_z = \omega \cos\vartheta, \sin\varphi$

dakle mo zna pisati

$$U = 2 \cdot \frac{V}{(2\pi)^3} \int \bar{E}(\vec{q})\, d^3\vec{q} \qquad \omega = \vec{q} \cdot c \;\Rightarrow\; d^3\vec{q} = \frac{1}{c^3} d^3\omega \;\to\; \frac{4\pi}{c^3} \omega^2 d\omega$$

$$U = \frac{V}{\pi^2 c^3} \int_0^\infty \bar{E}(\vec{q})\, \omega^2 d\omega$$

gustoća energije :

$$u = \frac{U}{V} = \int_0^\infty \underbrace{\frac{1}{\pi^2 c^3}\bar{E}(\varepsilon)\omega^2 d\omega}_{du} = \int_0^\infty u_\omega \, d\omega$$

doprinos rezonatora $\omega, \omega + d\omega$

$$du = \frac{\bar{E}(\varepsilon)\cdot\omega^2}{\pi^2 c^2} d\omega$$

→ iz ekvipartcije ravnoteže & harm. oscilatora & jednaka raspodj. energije ⇒ $\bar{E}(\varepsilon) = kT$ (energija jednog ravnoteže)

fja - spektralne raspodjele

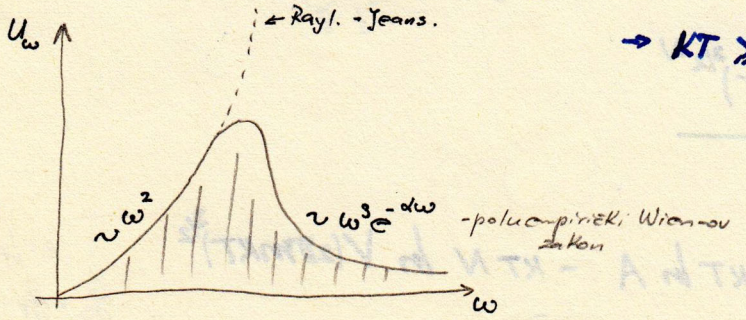
$$u_\omega = \frac{du}{d\omega} = \frac{\omega^2 kT}{\pi^2 c^3}$$

Rayleigh - Jeans (1900)

Koliko energije otpada na jedan interval frekv.

→ precjenjivanje doprinosa za velike frekvencije

→ eksp. slaganje za male frekvencije



→ $kT \gg \frac{\hbar}{2\pi} 2\pi\nu$

Što je općenito u slaganju da klas. slika vrijedi: dok je temp. dovoljno visoka

$$U = V\int_0^\infty \underbrace{\frac{du_\omega}{d\omega}}_{\to \omega^2} \cdot d\omega \to \infty$$

divergira u okvirima klas. fizike

„Ehrenfest" - ultravioletna katastrofa

→ eksp. fja. daje konačnu površinu - energiju !

Planck - $kT u_\omega$ na visokim ω ⇒ $U \sim T^4$

Entropija idealnog plina

$S = s \cdot N$

fja-particije $Z = A \int_\Gamma e^{-\beta H(q_1, \dots p_{3N}, a)} d\phi$ $\qquad \beta = \frac{1}{KT}$ $\qquad A = \frac{1}{N! \, h^{3N}}$

1-A $N \Rightarrow S = 3N$ $\qquad A \sim \frac{1}{h^{3N}}$

$d\phi = dq_1 \dots dq_{3N} \, dp_1 \dots dp_{3N}$

$H = \sum_{i=1}^{3N} \frac{p_i^2}{2m} + U$ $\qquad U = \begin{cases} 0 & \text{unutar } V \\ \infty & \text{granici } V \text{ \& izvan} \end{cases}$

N - raznoprnih molekula $\qquad Z = A \left(\iiint_V e^0 \, dq_1 dq_2 dq_3 \right)^N \left(\int_{-\infty}^{\infty} \iiint e^{-\beta \frac{p^2}{2m}} d^3p \right)^N$

$Z = A V^N \left(\int e^{-\beta \frac{p^2}{2m}} d^3p \right)^N$

$t^2 = \frac{\beta}{2m} p^2 \qquad dp = \sqrt{\frac{2m}{\beta}} \, dt$

$\int e^{-\frac{\beta p^2}{2m}} d^3p = 4\pi \int_0^\infty e^{-\frac{\beta p^2}{2m}} p^2 dp = 4\pi \left(\frac{2m}{\beta}\right)^{3/2} \underbrace{\int_0^\infty e^{-t^2} t^2 dt}_{\frac{1}{2}\cdot\frac{\sqrt{\pi}}{2}} = (2\pi m KT)^{3/2}$

$$Z = A V^N (2\pi m KT)^{3/2 N}$$

slob. energija

$$F = -KT \ln Z = -KT \ln A - KT N \ln V (2\pi m KT)^{3/2}$$

$\beta = \frac{1}{KT} \qquad T = \frac{1}{K\beta}$

$\frac{\partial}{\partial \beta} = \frac{\partial}{\partial T} \cdot \frac{\partial T}{\partial \beta} = -\frac{1}{K\beta^2} \frac{\partial}{\partial T}$

$$\bar{U} = \left(\frac{\partial \beta F}{\partial \beta} \right)_V = -\frac{\partial}{\partial \beta} \ln T^{3/2 N} = -\frac{3}{2} N \frac{\partial}{\partial \beta} \ln T = -\frac{3}{2} N \cdot \frac{1}{T} \cdot \frac{\partial}{\partial \beta} T = -\frac{3}{2} N \frac{1}{T} \cdot \left(-\frac{1}{K} K^2 T^2\right)$$

$$-\left(\frac{\partial}{\partial \beta} \ln Z\right)_V = \frac{3}{2} NKT$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_V = K \ln A + KN \ln V (2\pi m KT)^{3/2} + KTN \cdot T^{-\frac{3}{2}} \cdot \frac{3}{2} T^{\frac{1}{2}} = K \ln A + KN \left(\ln V (2\pi m KT)^{3/2} + \frac{3}{2} \right)$$

$$= K \left\{ \ln A + N \ln \left[V (2\pi m KT e)^{3/2} \right] \right\}$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{KTN}{V}$$

jba. stanja ideal. plina - ne ovisi o A

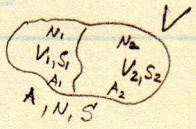
→ realno S ovisi o A, pa ovo je dobiti iz prom. entropije

→ posudu podijelimo (zamislimo) u dva dijela

aditivne veličine možemo zbrajati po dijelovima - kao entropiju

$$S_i = k\{\ln A_i + N_i \ln[V_i (2\pi m kT/e^2)^{3/2}]\}$$

$N_i \ln V_i + N_i \ln (2\pi m kT/e^2)^{3/2}$



$V = V_1 + V_2 \quad N = N_1 + N_2$ & $S = S_1 + S_2$ očekujemo zbog aditivnosti entropije

$$S_1 + S_2 = k\{\ln(A_1 A_2) + \ln(V_1^{N_1} \cdot V_2^{N_2}) + \underbrace{(N_1+N_2)}_{N} \ln(2\pi m kT/e^2)^{3/2}\}$$

$$- k\{\ln A + \ln V^N + N \ln(2\pi m kT/e^2)^{3/2}\} \quad / \ln \frac{V_1^{N_1} V_2^{N_2}}{V^{N_1} \cdot V^{N_2}}$$

$$\underline{S_1 + S_2 - S} = k \ln\left[\frac{A_1 A_2}{A} \cdot \left(\frac{V_1}{V}\right)^{N_1} \left(\frac{V_2}{V}\right)^{N_2}\right]$$

pretp.: $A = \frac{1}{h^{3N}} \quad A_1 = \frac{1}{h^{3N_1}} \quad A_2 = \frac{1}{h^{3N_2}}$

$$\frac{A_1 A_2}{A} = \frac{\frac{1}{h^{3(N_1+N_2)}}}{\frac{1}{h^{3N}}} = 1$$

$$\Rightarrow \underline{\frac{A_1 A_2}{A} = 1}$$

$$\underline{S_1 + S_2 - S} = k \ln\left[\left(\frac{V_1}{V}\right)^{N_1} \left(\frac{V_2}{V}\right)^{N_2}\right] \underline{< 0}$$

($\frac{V_1}{V} < 1$, $\frac{V_2}{V} < 1$)

Gibbs-ov paradox

→ Gibbs rješava:

pretp.: $A = \frac{1}{N! h^{3N}} \quad A_1 = \frac{1}{N_1! h^{3N_1}} \quad A_2 = \frac{1}{N_2! h^{3N_2}}$

Stirling: $N! \approx \left(\frac{N}{e}\right)^N$ za $N \gg 1$

$$A = \left(\frac{e}{h^3 N}\right)^N \quad A_1 = \left(\frac{e}{h^3 N_1}\right)^{N_1} \quad A_2 = \left(\frac{e}{h^3 N_2}\right)^{N_2} \Rightarrow \frac{A_1 A_2}{A} = \frac{N^N}{N_1^{N_1} N_2^{N_2}}$$

$$S_1 + S_2 - S = k \ln\left[\left(\frac{N V_1}{N_1 V}\right)^{N_1} \left(\frac{N V_2}{N_2 V}\right)^{N_2}\right]$$

jba. stanja na podsustavu: $pV = NkT$, $pV_1 = N_1 kT$, $pV_2 = N_2 kT$

$$\Rightarrow \frac{V}{V_1} = \frac{N}{N_1} \Rightarrow \frac{N V_1}{N_1 V} = 1 \qquad \frac{V}{V_2} = \frac{N}{N_2} \Rightarrow \frac{N V_2}{N_2 V} = 1 \Rightarrow$$

$$\Rightarrow \underline{S_1 + S_2 = S}$$

→ fizičko značenje uvučenih $N!$?

$$A = \frac{1}{N!h^{3N}} = \left(\frac{e}{Nh^3}\right)^N$$

$Z \quad Z = z^N$

$$S = Nk \ln\left[\frac{V(2\pi mkT)^{3/2} \cdot e^{5/2}}{Nh^3}\right]$$

1913. Sackur Tetrode

str. (9) $z = \frac{1}{h^3 N} \int_r e^{-\beta E} d\phi_m$ (*)

za $T \to 0$ logaritamski singularitet

⇒ ne zadovoljava III z. t. d. budući je S formalno izvedena u okvirima klas. statistike ↔ područja visokih temp.

$$S' = k \ln\left\{\frac{1}{N!}\left[\frac{V(2\pi mkT)^{3/2}}{h^3}\right]^N\right\}$$

$$(*) \Rightarrow S' = Nk \ln\left\{\frac{V(\quad)^{3/2} \cdot e^{3/2}}{\frac{N}{e} \cdot h^3}\right\}$$

Diskusija: $S = k \ln\left\{\frac{1}{N!}\right\}$

→ Boltzmann-ova rasp. opis. ponaš. idealnog plina

1. 2. čestice

$g_1 g_2$ 1. č. u g_1 2. č. u g_2

$g_2 g_1$ 1. č. u g_2 2. č. u g_1

raslik. čestica

varijacije s ponavljanjem

$N_i = 2$ $g_1 g_1$ $g_1 g_2$ $g_1 g_3$ ⋯ $g_1 g_i$

$g_2 g_1$ $g_2 g_2$ ⋯ $g_2 g_i$ g_i^2

$g_i g_1$ $g_i g_i$

broj različitih razmještaja molekula po energ. nivoima

$N_i = g_i e^{-\alpha - \beta E_i}$ $S = k \ln B$

$S' = k[N \ln N + (1+N)N + (-1-\alpha)\beta \sum_i N_i E_i$

E_2 N_2 g_2

E_1 N_1 g_1

$$B = N! \prod_i \frac{g_i^{N_i}}{N_i!}$$

Boltzmann-ova relacija $S = k \ln B$ ← t-dm. vjerojatnost

1. 2. N_i čestice

$g_1 g_1 g_2 g_2 - g_3 \cdots g_{i-1} g_{i-1} g_i$

⇒ Korekcija prebrojavanja

$$B = \prod_i \frac{g_i^{N_i}}{N_i!}$$

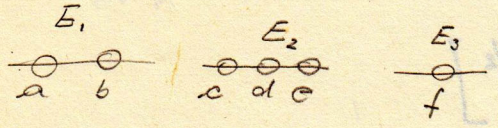
(!) pravo prebroj. stanja mora dovesti do tog rezultata

nije dovoljno, ispravo previše podijelili sa $N!$

→ doseod pretp. da permutacije čestica na različ. energ. nivoima → novom raspodjelom

→ iz osnovnog postulata Klas. fizike : $q_i(t_0)$ $p_i(t_0)$ / $q_i(t)$ $p_i(t)$ } $i = 1, \ldots 3N$ strogo određeni

⇒ možemo pratiti kretanje čestica pa ih i međusobno razlikovati.



↳ Uveli smo pretp. da su jednake čestice (masa, spin) međusobno razlučive i dobili $N!$

a budući se $N!$ ne smije pojaviti izlazi da

→ jednake čestice nemožemo međusobno razlikovati - osnovni postulat Kvantne stat. fizike

$\Delta p \cdot \Delta q \approx h$ ↑ čestica razmazana u faznom prostoru, pa ih ne možemo dovoljno dobro slijediti.

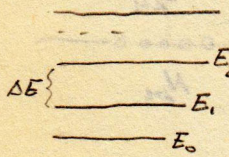
- ograničenje područja Kl. stat. fiz.

uz (36) (*) Idio

Fazni prostor $\phi_1(\Gamma)$ razbijemo na područja istih energija E_i

$$g(\varepsilon) = \frac{\omega(\varepsilon)}{h^s} d\varepsilon$$

$E_i \leftrightarrow \Omega_i(E_i)$ $\quad g_i = \frac{\Omega_i(E_i)}{h^3}$ $\quad \frac{\Omega_i(E_i)}{h^s}$ gdje s-br. st. slobode molekule (čestice)



za 1-A plin, elem. čestice itd.

$$H = \frac{1}{2m}(p_1^2 + \dots p_s^2) + E_p(q_1, \dots q_s)$$

$$\Omega_i(E_i) = \phi(E_i) = \int_{(H=E_i)} dq_1 \dots dq_s\, dp_1 \dots dp_s$$

za $\Delta E \to 0$ kontinuir. spektar energija

$$= \int_M \delta[E_i - H(q_1, \dots p_s)]\, dq_1 \dots dp_s$$

N_i čestica u i-tom području E_i sa g_i ćelija

1 2 3 4 5 N_i $\qquad$ $N_i - 1$ N_i $\qquad$ N_i / g_i / $N_i!$

(*) $q_1 q_1 q_1 q_2 q_2 q_4 q_4 \dots q_{i-1} q_{i-1} q_i q_i$

ili

(**) $q_1\,123\,q_2\,45\,q_3\,q_4\,67 \dots q_{i-1}\,(N_i-3)\,(N_i-2)\,q_i\,(N_i-1)\,N_i$

$q_1 q_1 \; q_1 q_2 \; q_1 q_3 \dots q_1 q_i$
$q_2 q_1 \; q_2 q_2 \dots q_2 q_i$
$q_i q_1 \qquad q_i q_i$

$q_1 q_1 q_1 \; q_1 q_1 q_2 \dots q_1 q_1 q_i$
$q_1 q_1 \qquad q_1 q_i q_1 \qquad q_1 q_i q_i$

(*) U g_i ćelija pruža mogućnost različitih novih načina rasporeda N_i čestica na tih g_i ćelija unutar nivoa E_i

(ista ćelija više puta se može popuniti)

$g_i^{N_i}$ ukupan broj varijacija sponavljanjem od g_i elemenata N_i-reda tj. s tim da

Kao različiti slučaji se uzima ako je 5 čestica u g_2 ili u nekoj drugoj ćeliji

recimo u g_1, drugačije rečeno uzima se da je različ. slučaj ako su u g_2 4 i 5 čestica ili 3 i 4 čestica

1 2 3 4 5 / $q_1 q_1 q_2 q_2 q_1 \; q_4 q_4 \dots q_{i-1} q_{i-1} q_i q_i$ / N_i

$\Rightarrow$ što proizlazi iz pretp. da jednake čestice razlikujemo

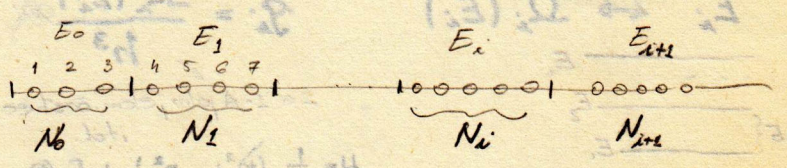
$\frac{g_i^{N_i}}{N_i!}$ - dijeljenje sa $N_i!$ je prevelika budući nemalo broj permutacija u slučaju ako se jedna ćelija pavlja više puta (tj. više čestica u 1 ćeliji) već bi trebalo dijeliti sa (u kombinatornom slučaju) $\frac{N_i!}{3!\,2!\,0!\,2! \dots 2!\,2!}$

tako da to nije rezultat kao u slučaju kombinacija sponavljanjem, već manji

Klas. stat. - fizika

Boltzmann-ova statistika raspodjela: - razlikovanje čestica

N - čestica



E_4 ——

E_3 - - -

E_2 ——

E_1 ——

E_0 ——

→ broj mogućih razmještaja N-čestica na energ. nivoe $E_0, E_1, \dots E_i, \dots$

(čestica nosi svoj broj - odnosno položaj i impuls)

$(\alpha_j)_k$ j-ta molekula na k-tom položaju

(pridruživanje $j \leftrightarrow k$) za N! permutacija

⇒ $N!$ ukupan broj permutacija

među tim permutacijama su permutacije koje se sastoje od permutacije čestica samo na položajima unutar nekog i-tog nivoa, što ne daje fizikalno nešto novo, nego: težimo samo za tim da su prisutni:

$$\frac{N!}{N_0!\, N_1! \cdots N_i! \cdots} = N! \prod_i \frac{1}{N_i!}$$

→ broj mogućnosti da N mol. dođe samo u nivoe $E_0, E_1, \dots E_i, \dots$

tj. glavno da su prisutni

↑ taj faktor dobivamo samo u slučaju da jednake čestice smo u stanju razlikovati

$g_i^{N_i}$ - broj mogućnosti raspored N_i čestica na g_i ćelija unutar nivoa E_i uslučaju kad čestice med. razlikujemo tj. razlikujemo da li je u g_2 1 & 2 čestica ili 1 & 3 čestica

⇒ varijacije s ponavljanjem

⇒ $$B = N! \prod_i \frac{g_i^{N_i}}{N_i!}$$

(naravno uvjek)

$$\sum_i N_i E_i = U \qquad \sum_i N_i = N$$

Entropija i fazni volumen

1-A $N \Rightarrow 6N$-dim.

$H \Leftrightarrow U \Leftrightarrow E$

$$d\phi = dq_1 \dots dq_{3N}\, dp_1 \dots dp_{3N}$$

$$H = \frac{1}{2m}(p_1^2 + \dots + p_{3N}^2) + E_p(q_1, \dots q_{3N})$$

bitno! $H \leq U$ (*) time je definiran i fazni volumen koji želimo povezati s $H \leq U$

$\Gamma(E)$ ← fazni volumen koji je pridružen H-U

$$\Gamma(H) = \Gamma(U) = \Phi(H) = \int_{\Gamma_{H\leq U}(*)} dq_1 \dots dq_{3N}\, dp_1 \dots dp_{3N}$$

$\Gamma_{H\leq U}(*)$ – tj. integracija po onim slogovima $(q_1, \dots p_{3N})$ koji daju $H \leq U$

$$\int_\Gamma \delta[U - H(q_1, \dots p_{3N}, a)]\, d\phi = \Omega(U, a) \quad \text{bolje} \quad \Omega(H, a)$$

$$d\Gamma(E) = \frac{d\Gamma(E)}{dE} dE = \Omega(E, a)\, dE$$

$\Omega(E, a)$ veličina energetske ljuske

$$d\phi = dq_1 \int_{=S^{3-1}} \dots \int \prod_{i=1}^{3N} dq_i \, dq_{3N}$$

$$dW = \alpha \cdot \varrho\, d\phi = w \cdot d\phi$$

$$F = \psi = -\theta \ln Z = -\frac{1}{\beta} \ln Z \Rightarrow \frac{1}{Z} = e^{\beta F}$$

zapravo $w = \varrho = A \cdot \frac{1}{Z} e^{-\beta H} = A\, e^{\beta(F-H)}$ $\qquad \beta = \frac{1}{kT}$

$\to^{za}\ \alpha = 1$, $\varrho \equiv w$

$$\int_\Gamma dW = 1 \Rightarrow \alpha \int_\Gamma \varrho\, d\phi = 1 \qquad \alpha A \frac{1}{Z} \int_\Gamma e^{-\beta H} d\phi = 1 \Rightarrow Z = \alpha A \int_\Gamma e^{-\beta H} d\phi$$

$$\int_\Gamma dW = 1 \Rightarrow \alpha A \int_\Gamma e^{\beta(F-H)} d\phi = 1$$

$$A = \frac{1}{N!\, h^{3N}} \overset{N \gg 1}{\approx} \frac{e^N}{N^N h^{3N}} = \left(\frac{e}{Nh^3}\right)^N$$

↑ izbjegli Gibbs-ov paradox

integracija po Γ → integracija po energiji:

$$d\phi = \frac{d\phi(H)}{dH} dH$$

F – termodin. veličina neovisi o $d\phi$

$$A e^{\beta F} \int_{(H)} e^{-\beta H} \frac{d\phi}{dH} dH = 1$$

$$\Rightarrow dW^{(H)} = A e^{\beta F} e^{-\beta H} \frac{d\phi^{(H)}}{dH} dH = A e^{\beta F} P(H) dH$$

$\Omega(H, a)$, $P(H) = e^{-\beta H} \frac{d\phi^{(H)}}{dH}$

→ analiza se svodi na proučavanje fje. vjerojatnosti $P(H)$, koja bitno ovisi o faznom volumenu pridruženom H

$$1 = \int_{(E)} W(E)\, dE \qquad dW = W(E)\, dE$$

$$A = \frac{1}{N!\, h^s}$$

$$W(E) = \int_\Gamma \delta[E - H(q_1, \dots p_s, a)]\, A\, e^{\frac{1}{\theta}[\psi - H(q_1, \dots p_s, a)]}\, d\phi$$

$$= A\, e^{\frac{\psi - E}{\theta}} \Omega(E, a)$$

$$= A \cdot \frac{1}{Z} e^{-\frac{E}{\theta}} \Omega(E, a)$$

$$Z = A \int_{(E)} e^{-\frac{E}{\theta}} \Omega(E, a)\, dE$$

$$W(E) = \underbrace{A e^{\frac{\psi}{\theta}}}_{\frac{1}{Z}} e^{-\frac{E}{\theta}} \Omega(E) = A e^{\beta F} P(E)$$

spec.: 1-A **idealni** plin

$$\phi(E) = V^N \cdot \text{Konst.} \cdot (2mE)^{\frac{3N}{2}}$$

$$\frac{d\phi(E)}{dE} = \text{Konst.} \cdot (2m_E)^{\frac{3N}{2}} \cdot V^N \cdot E^{\frac{3N}{2}-1}$$

$$\phi(H) \sim H^{\frac{3}{2}N}$$

$N \gg 1$ $\Rightarrow$ vrlo brzo raste (tj. promatramo što se događa kako jako povećavamo broj čestica)

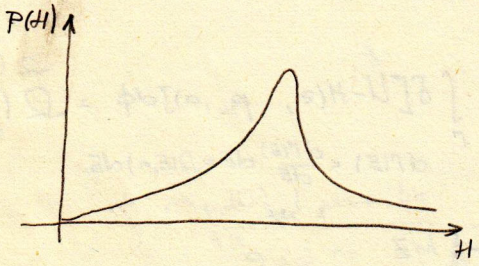
to približno vrijedi i za realni plin (dokazati ćemo)

$\Rightarrow$ $\phi(H) \sim H^{n+1}$ ($n+1$ visoka potencija) $\Rightarrow$ $\frac{d\phi}{dH} \sim H^n$

$$P(H) = e^{-\beta H} \frac{d\phi(H)}{dH} \sim e^{-\beta H} \cdot H^n$$

padajući dio za H — rastući dio za H

$\rightarrow$ fja. ima singularitet za max. u sustavu (ekstrem)



$f(x) = e^{-x} x^n$ $\quad n \gg 1$ ili $n \to \infty$

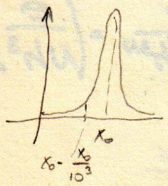
max. fje. $f(x)$:

$$\frac{df}{dx} = e^{-x_0}(-x_0^n + n x_0^{n-1}) = 0 \quad \Rightarrow \quad x_0 = n \quad \Rightarrow f(x_0) = e^{-x_0} x_0^{x_0}$$

$x_0 - \frac{x_0}{10^3} = 0{,}999\, x_0$

$x_0 + \frac{x_0}{10^3} = 1{,}001\, x_0$

maximum $f(x)$ za $X = x_0,\ x_0 - \frac{x_0}{10^3},\ x_0 + \frac{x_0}{10^3}$ (tj. $0{,}999\,x_0$, $1{,}001\,x_0$)



$$\frac{f(0{,}999\,x_0)}{f(x_0)} = \frac{e^{-0{,}999x_0} \cdot (0{,}999x_0)^n}{e^{-x_0} \cdot x_0^n} = 10^{-0{,}000000217\,3\, x_0}$$

$$\log\left[\left(e^{-0{,}999}\right)^{x_0} \cdot 0{,}999^{x_0}\right] = 0{,}001\, x_0 \log e + x_0 \cdot \log 0{,}999 = 0{,}000\,434\,29\, x_0 + x_0(-1 + 0{,}999\,57) = (0{,}000\,434\,29 - 1)\, x_0 = -$$

(zbog primjene Taylora 6.)

$$\frac{f(1{,}001\,x_0)}{f(x_0)} = \frac{e^{-1{,}001\,x_0} \cdot (1{,}001\,x_0)^n}{e^{-x_0} \cdot x_0^n} = 10^{-0{,}000000217\,0\, x_0}$$

za $x_0 = n = 10^8$ $\Rightarrow$ $\frac{f(0{,}999 \cdot 10^8)}{f(10^8)} = 10^{-21{,}73} \to 0$ strmi maximum

$\rightarrow$ druga metoda: ispitivanje strmine

$$f(x) = e^{-x + n \ln x} \qquad f(x_0 + \Delta x) = e^{-(x_0 + \Delta x) + n \ln(x_0 + \Delta x)}$$

$$\ln(x_0 + \Delta x) = \ln\left[x_0\left(1 + \frac{\Delta x}{x_0}\right)\right] = \ln x_0 + \ln\left(1 + \frac{\Delta x}{x_0}\right) = \ln x_0 + \frac{\Delta x}{x_0} - \frac{1}{2}\left(\frac{\Delta x}{x_0}\right)^2 + \frac{1}{3}\left(\frac{\Delta x}{x_0}\right)^3 - \frac{1}{4}\left(\frac{\Delta x}{x_0}\right) + \ldots$$

za $-1 < \frac{\Delta x}{x_0} \leq 1$

$\Delta x \ll x_0$ $\Rightarrow$ $f(x_0 + \Delta x) \approx e^{-(x_0 + \Delta x) + n \ln x_0 + n \frac{\Delta x}{x_0} - \frac{n}{2}\left(\frac{\Delta x}{x_0}\right)^2} =$

$$= e^{-x_0 + n \ln x_0 - \frac{n}{2}\left(\frac{\Delta x}{x_0}\right)^2}$$

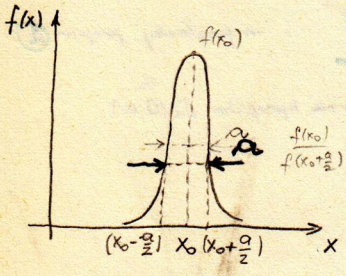
$\Delta x \ll x_0$

(*) $f(x_0+\Delta x) = f(x_0)\cdot e^{-\frac{n}{2}\left(\frac{\Delta x}{x_0}\right)^2} = f(x_0)\cdot e^{-\frac{(\Delta x)^2}{2x_0}}$

$\frac{f(x_0+\Delta x)}{f(x_0)} = e^{-\frac{1}{2}\left(\frac{\Delta x}{x_0}\right)^2\cdot n}$ ($\to 1$)

$\Rightarrow (\exists n_0)(\forall n > n_0)\left(\frac{f(x_0+\Delta x)}{f(x_0)} < \varepsilon \ll 1\right)$

, a to smo pokazali i numerički



$2f\left(x_0+\frac{a}{2}\right) = f(x_0)$

$\frac{f(x_0)}{f(x_0+\frac{a}{2})} = e \approx 2{,}71$

Def: Širina maximuma $\to a$

$f\left(x_0+\frac{a}{2}\right) = \frac{f(x_0)}{e}$ (Δx, $:2$)

$e^{-1} = e^{-\frac{n}{2}\left(\frac{a}{2x_0}\right)^2}$

$\frac{n}{2}\left(\frac{a}{2x_0}\right)^2 = 1$

$\frac{a}{2x_0} = \sqrt{\frac{2}{n}}$

(*) $\Rightarrow$ $\boxed{\frac{a}{x_0} = 2\cdot\sqrt{\frac{2}{n}}}$

relativna širina maximuma

$\frac{a}{f(x_0)} = \frac{2x_0\sqrt{\frac{2}{n}}}{e^{-x_0}x_0^n} = \frac{2\sqrt{2}\cdot n\, n^{-1/2}}{e^n\cdot n^n}$

$N! \approx \left(\frac{N}{e}\right)^N \quad N \gg 1$

$= 2\sqrt{2}\cdot\frac{e^n}{n^{n-1/2}} = 2\sqrt{2}\cdot\frac{n^{1/2}}{\left(\frac{n}{e}\right)^n}$

$\lim_{n\to\infty}\frac{a}{f(x_0)} = 2\sqrt{2}\lim_{n\to\infty}\frac{n^{1/2}}{n!} = 0$

→ Mikrokanonski ansambl - sv. članovi (sistemi koji ulaze u ansambl) moraju biti na energetskoj hiperplohi

⇒ Kanonski ansambl ≈ Mikrokanonski za velik broj sustava (čestica) rasipanje $\sim \frac{1}{\sqrt{N}}$ neznatno

Posljedice za izračunavanje sr. vrj. t-dm. veličina

$dW = A e^{\beta F} e^{-\beta H}\frac{d\phi}{dH}dH = \frac{P(H)dH}{\int_{(H)} P(H)dH}$ ($\int_{(H)} dW = 1$, $P(H)$)

$W(E) = A e^{\beta F} P(E)$ za $N\to\infty$ $W(E) = \delta(E-E_0)$

ili $W(H) = \delta(H-H_m)$

$\bar{G}_{(H)} = \int_\Gamma G\,dW = \int_\Gamma G\,\underbrace{e^{\beta F}e^{-\beta H}}_{\text{const. u } W}\,d\phi = A e^{\beta F}\int_\Gamma G e^{-\beta H}d\phi = \frac{\int_\Gamma G e^{-\beta H}d\phi}{\int_\Gamma e^{-\beta H}d\phi}$

$d\phi = \frac{d\phi(H)}{dH}dH$

$P(H) = e^{\beta H}\frac{d\phi(H)}{dH}$

$A = \frac{1}{N!\,h^{3N}}$

$\Rightarrow$ $\boxed{\bar{G}_{(H)} = \frac{A e^{\beta F}\int_{(H)} G\,P(H)dH}{A e^{\beta F}\int_{(H)} P(H)dH}}$ ($\int_\Gamma e^{-\beta H}d\phi = \frac{1}{A e^{\beta F}}$)

$P(H) = \frac{1}{A e^{\beta F}}W(H)$ $\quad W(H)\to\delta(H-H_m)$

$dW = W(H)dH$ $\quad \int_{(H)} W(H)dH = 1 \Rightarrow \int_{(H)}\delta(H-H_m)dH = 1$

$\Rightarrow \bar{G}_{(H)} = \frac{\int_{(H)} G\,W(H)dH}{\int_{(H)} W(H)dH} = \int_{(H)} G(H)\,\delta(H-H_m)dH = G(H_m)$

$\Rightarrow$ $\boxed{P(H) = \frac{1}{A e^{\beta F}}\delta(H-H_m)}$ (**) singularna f/ja.

$\Rightarrow$ $\boxed{\bar{G}(H) = G(H_m)}$ (*) - u vrlo dobroj aproksimaciji: jer zbog (*) u energetskom spektru značajan doprinos samo za $H = U_{max}$ (termodinamički)

ili: $\bar{G}_{(H)} = \int_{(H)} G(H)dW^{(H)} = \int_{(H)} G A e^{\beta F}P(H)dH = A e^{\beta F}\int_{(H)} G\,P(H)dH = \int_{(H)} G(H)\cdot\delta(H-H_m)dH = G(H_m)$

$H = U$

$U_1 = H(q_1, \dots p_{3s}, a)$

$U_{2s} = U_{2s}(q_1, \dots p_{3s}, a)$

(22) a) $\Rightarrow$ Mikrokan. ansambl

$$\bar{U} = \bar{H} = \int_\Gamma H dW = \frac{1}{\Omega(U_m, a)} \int_\Gamma H \, \delta[H(q_1, \dots p_{3s}, a) - U_m] d\phi = \frac{1}{\Omega(U, a)} \int_{2s} \int U_1 \delta(U_1 - U_m) J(U_1, \dots U_{2s}) \cdot dU_1 \cdot dU_2 \dots dU_{2s}$$

$$= \frac{1}{\Omega(U_m, a)} U_m \left(\int_{2s-1} \dots \int [J]_{U_1 = U_m} dU_2 \dots dU_{2s} \right) = \frac{U_m \cdot \Omega(U_m, a)}{\Omega(U_m, a)}$$

(*) $\Rightarrow$ $\bar{U} \approx U_m$ najvjerojatnija energija sustava $\approx$ sr. energiji sustava

$$dW = A e^{\beta F} e^{-\beta H} = A \frac{1}{Z} e^{-\beta H}$$

$$Z = e^{-\beta F} = A \int_\Gamma e^{-\beta H} d\phi$$

Particiona fja.

$$Z = A \int_\Gamma e^{-\beta H} d\phi(H) = A \int_0^\infty e^{-\beta H} \Omega(H) dH \overset{\text{aprox}}{\approx} A e^{-\beta \bar{U}} \phi(\bar{U})$$

zaprav. $= A e^{-\beta U_m} \cdot \phi(U_m)$

$\phi(\bar{U})$ - volumen oko hiperplohe $\Omega(\bar{U}, a)$ U_m

$\rightarrow$ pogledaj papir (1.)

što je u skladu sa: $U_m \approx \bar{U} = -\frac{\partial}{\partial \beta} (\ln Z)_V = U_m$

$\rightarrow$ singularni karakter fje. vjerojatnosti. Omogućava da na jeftin način izračunamo sve t-din. veličine

$Z = A \int_\Gamma e^{-\beta H} d\phi$ A - se pogađa da se vidi broj stanja u $d\phi$ s energijom H

$$\sum_i g_i = \text{broj stanja} = \int \frac{d\phi}{h^s}$$

$\rightarrow$ veza statist. fizika - t.dinamika

statist.: $F = -kT \ln Z = -kT [-\beta \bar{U} + \ln A\phi(\bar{U})] =$

$= \bar{U} - kT \ln A\phi(\bar{U})$

t.-din.: $F = U - TS$

$\Rightarrow$

$$\Rightarrow \quad S = k \ln (A\phi(\bar{U})) \quad \text{- Boltzmann-ova relacija}$$

(B)

$$A\phi(\bar{U}) = \frac{1}{N!} \frac{\phi(\bar{U})}{h^s}$$

broj mikroskop. stanja iste energije $\bar{U}$ (uz samu hiperplohu $H = \bar{U}$)

tj. statistička težina stanja u sr. vrij.

$\downarrow$

zaprav. kod. Kanonske to je strogo $\frac{\Omega(E, a)}{h^s} = g(E)$

$\rightarrow$ Kod realnog plina isti rezultat

Napomena!!! (A) u izrazu za Z $\phi(\bar{U})$ nije fazni volumen u smislu $\phi(H) = \int_0^H \Omega(H) dH$

već samo fazni volumen oko hiperplohe $\Omega(\bar{U}, a)$ zbog odstupanja

(A) reda veličine h^s - fazne ćelije

usrednjeno po kan. ansamblu

napomena: na (24) c) općenito izvedeno $S = -k(\overline{\ln W} + \ln N! h^s) = -k(\overline{\ln W} + \ln N! h^s) = k \ln \left(\frac{1}{N! h^s W} \right)$

$W \equiv g = A e^{\beta F} \cdot e^{-\beta H} \xrightarrow{N \gg} \frac{1}{\Omega(U_m, a)} \delta[H - U_m]$

(1) (38)

$H = H(q_1 \dots p_s, A)$

$$Z = A \int_\Gamma e^{-\beta H} d\phi$$

$u_1 = H(q_1, \dots p_s, A)$

u_2

$\vdots$

$u_{2s} = u_{2s}(q_1, \dots p_s, A)$

$$= A \int_0^\infty \cdots \int_{2s} e^{-\beta u_1} \cdot J \, du_1 \dots du_{2s}$$

$$J = \frac{\partial(q_1, \dots p_s)}{\partial(u_1, \dots u_{2s})}$$

$J(u_1, \dots u_{2s})$

$$= A \int_0^\infty e^{-\beta u_1} \underbrace{\left[\int_{2s-1} \cdots \int_{u_1 \le H} J \, du_2 \dots du_{2s} \right]}_{\Omega(u_1)} du_1$$

$$= A \int_0^\infty e^{-\beta H_1} \Omega(H_1) \, dH_1$$

$$\phi(H) = \int_0^H \Omega(H) dH$$

$$\phi(0) = 0$$

$$= A \int_0^\infty \underbrace{e^{-\beta H}}_{u} \underbrace{\Omega(H) dH}_{dv} \qquad \frac{d\phi(H)}{dH}$$

$$du = -\beta e^{-\beta H} dH$$

$$v = \int_0^H \Omega(H) dH = \phi(H)$$

$$= A \left[\left(e^{-\beta H} \cdot \int_0^H \Omega(H) dH \right)_0^\infty + \beta \int_0^\infty e^{-\beta H} \phi(H) dH \right]$$

$$\lim_{H \to \infty} e^{-\beta H} \int_0^H \Omega(H) dH = \lim_{H \to \infty} e^{-\beta H} \phi(H) = 0$$

$$e^{-\beta \cdot 0} \cdot \phi(0) = 1 \cdot \phi(0) = 0$$

$$= A \cdot \beta \int_0^\infty e^{-\beta H} \phi(H) dH$$

$$\overset{?}{=} \int_0^\infty A e^{-\beta H} \phi(H) \, \delta(H - \bar{u}) \, dH$$

$$\phi(E) = \int_{H \le E} d\phi =$$

$$H(q_1, \dots p_s, a) = u_1$$

$$u_2$$

$$\dots$$

$$u_{2s}$$

$$\Rightarrow J = \frac{\partial(q_1, \dots p_s)}{\partial(u_1, \dots u_{2s})} \neq 0$$

$$H \le E \Rightarrow u_1 \le E$$

$$\phi(E) = \int_0^E \dots \left[\int_{2s-1} \dots \int [J]_{u_1} du_2, \dots du_{2s} \right] du_1$$

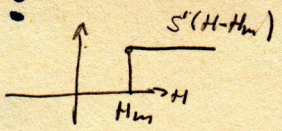
$$= \int_0^E \Omega(u_1)\, du_1$$

$$\Omega(H) = \int_{2s-1} \dots \int [J]_{u_1 = H} du_2 \dots du_{2s}$$

$$\therefore \phi(H) = \int_0^H \Omega(H)\, dH$$

$$\int_0^\infty A e^{-\beta H} \phi(H) \underbrace{\delta(H-H_m)\,dH}_{dV} =$$

$$\phi(H) = \int_0^H \Omega(H)\,dH$$



$$= \Big[\underbrace{A e^{-\beta H} \phi(H)\, \delta'(H-H_m)}_{=0} \Big]_0^\infty \qquad \phi(0) = 0$$

$$- \int_0^\infty A \left[-\beta e^{-\beta H} \phi(H) + e^{-\beta H} \frac{d\phi(H)}{dH} \right] \delta(H-H_m)\,dH$$

$$= A\beta \int_0^\infty e^{-\beta H} \phi(H)\, \delta'(H-H_m)\,dH \qquad - A \int_0^\infty e^{-\beta H} \Omega(H)\, \delta'(H-H_m)\,dH$$

$$= A\beta \int_{H_m}^\infty e^{-\beta H} \phi(H)\,dH \qquad - A \int_{H_m}^\infty e^{-\beta H} \Omega(H)\,dH$$

$$= A\beta \int_0^\infty e^{-\beta H} \phi(H)\,dH - A\beta \int_0^{H_m} e^{-\beta H} \phi(H)\,dH$$

1-A idealan plin N $6N$-dim.

$$\phi(H) = \int_{r(H\le U)} dq_1 \dots dq_{3N}\, dp_1 \dots dp_{3N} = \left(\iiint_V dq_1\, dq_2\, dq_3\right)^N \int_{H\le U} dp_1 \dots dp_{3N}$$

$$H = \frac{1}{2m}\left(p_1^2 + p_2^2 + \dots + p_{3N}^2\right)$$ jba. hiperkugle $R^2 = 2mH$

$$\phi(H) = V^N \int_{H\le U} dp_1 \dots dp_{3N}$$

volumen kugle:

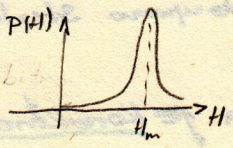
$$\int_{H\le U} dp_1 \dots dp_{3N} \sim R^{3N} \qquad R = (2mH)^{1/2}$$

$$\underline{\phi(H) = V^N \cdot C_{const.} \cdot R^{3N} = V^N \cdot C\,(2mH)^{\frac{3N}{2}}}$$

$P(H) = e^{-\beta H} \frac{d\phi(H)}{dH}$

$$\frac{d\phi(H)}{dH} = 3Nm\,C\,V^N\,(2mH)^{\frac{3N}{2}-1}$$

$$\underline{P(H) = 3Nm\,C\,V^N e^{-\beta H}(2mH)^{\frac{3N}{2}-1}}$$



$P(H)$ bitno $\neq 0$ uskom području oko H_m

→ energetski maximumum $H = U_m$

$$0 = \frac{dP(H)}{dH} = 3NmCV^N\left[-\beta e^{-\beta H} H^{\frac{3N}{2}-1} + \left(\tfrac{3N}{2}-1\right) e^{-\beta H} H^{\frac{3N}{2}-2}\right](2m)^{\frac{3N}{2}-1}$$

$$= 3NmCV^N(2m)^{\frac{3N}{2}-1}\, e^{-\beta H} H^{\frac{3N}{2}-2}\left[-\beta H + \left(\tfrac{3N}{2}-1\right)\right] \Rightarrow H_1 = 0,\ H_2 = \infty$$

$$\Rightarrow H = U_m = \left(\tfrac{3N}{2}-1\right)KT \overset{N\gg 1}{\approx} \tfrac{3}{2}NKT$$

$$\underline{\bar{U} = U_m = \tfrac{3}{2}NKT}$$ $\bar{U} = U_m$ u makroskop. sistemu

$\phi(U_m)$

$$\Rightarrow \phi(\bar{U}) = V^N \cdot C\,(3mNKT)^{\frac{3N}{2}}$$

→ procjena (38) aproks. Kod integriranja za particioni fju. $Z = A\int e^{-\beta H} d\phi = Ae^{-\beta\bar{U}} \cdot \phi(\bar{U})$

$$\underline{Z \approx A e^{-\beta\bar{U}} \phi(\bar{U}) = AC V^N e^{-\frac{3N}{2}} \cdot (3NmKT)^{\frac{3N}{2}}} \quad (*)$$

iz $\bar{E} = -KT\ln Z$

$S = K\ln(A\phi(\bar{U}))$.

$$\underline{S = K \ln\left[AC V^N (3NmKT)^{\frac{3N}{2}}\right]}$$

nastavak (38)

$$\phi(H) = \int_0^H \Omega(H)\,dH \qquad \Omega(H) = \frac{d\phi(H)}{dH}$$

$$\frac{d\phi(H)}{dH} = 3Nm\,CV^N (2mH)^{\frac{3N}{2}-1}$$

$$= \frac{3N}{2}(2m)\cdot CV^N (2m)^{\frac{3N}{2}-1}\cdot H^{\frac{3N}{2}-1}$$

egzaktno:

$$= A\int_0^\infty e^{-\beta H}\Omega(H)\,dH$$

$$Z = A\int_\Gamma e^{-\beta H}\,d\phi = A\int_0^\infty e^{-\beta H}\frac{d\phi(H)}{dH}\,dH = \frac{3N}{2}ACV^N(2m)^{\frac{3N}{2}}\int_0^\infty e^{-\beta H}H^{\frac{3N}{2}-1}\,dH$$

$$= \frac{3N}{2}ACV^N(2mKT)^{\frac{3N}{2}}\int_0^\infty e^{-t}t^{\frac{3N}{2}-1}\,dt$$

$\beta H = t \Rightarrow H^{\frac{3N}{2}-1} = \left(\frac{1}{\beta}\right)^{\frac{3N}{2}-1}\cdot t^{\frac{3N}{2}-1}$

$dH = \frac{1}{\beta}\,dt$

pretp. $N = 2n$ — N-paran, za Z nije bitno

$$\int_0^\infty e^{-t}\cdot t^{3n-1}\,dt = \Gamma(3n) = (3n-1)! = \left(\frac{3N}{2}-1\right)!$$

$N = 2m+1$

$$\int_0^\infty e^{-t}\,t^{\frac{6m+3}{2}-1}\,dt = \Gamma\left(\frac{6m+3}{2}\right) = \Gamma\left(\frac{2(3m+1)+1}{2}\right) = \frac{(2(3m+1))!}{2^{2(3m+1)}\cdot(3m+1)!}\sqrt{\pi} = \frac{(3N-1)!}{2^{3N-1}\cdot\left(\frac{3N-3}{2}-1\right)!}\sqrt{\pi}$$

$$Z = ACV^N(2mKT)^{\frac{3N}{2}}\cdot\left(\frac{3N}{2}\right)! = A e^{-\beta\bar{U}}\phi(\bar{U}) \quad (**)$$

$\Rightarrow$ za idealni plin dokazano

$$1 = \int_\Gamma \varrho\,d\phi = \varrho(\bar{U})\phi(\bar{U})$$

$$Z = ACV^N e^{-\frac{3N}{2}}(3NmKT)^{\frac{3N}{2}} = ACV^N\cdot(2mKT)^{\frac{3N}{2}}\cdot e^{-\frac{3N}{2}}\left(\frac{3N}{2}\right)^{\frac{3N}{2}}$$

$\rightarrow$ (*) & (**) su isti ako $\left(\frac{3N}{2}\right)! = e^{-\frac{3N}{2}}\left(\frac{3N}{2}\right)^{\frac{3N}{2}} = \left(\frac{\frac{3N}{2}}{e}\right)^{\frac{3N}{2}}$

a to je upravo Stirling-ova formula koja vrijedi za $N \gg 1$

$\Rightarrow$ Opravdana je **korektnost aproksimacije** za $Z \approx Ae^{-\beta\bar{U}}\phi(\bar{U})$ na (38)

(35) str.

(*) $\Rightarrow$ $Z = ACV^N e^{-\frac{3N}{2}}(3NmKT)^{\frac{3N}{2}}$ $\qquad Z = AV^N(2\pi mKT)^{\frac{3N}{2}}$ $\qquad A = \frac{1}{N!\,h^{3N}} \overset{N\gg1}{=} \left(\frac{e}{Nh^3}\right)^N$

$= AV^N(2\pi mKT)^{\frac{3N}{2}}\cdot C\cdot e^{-\frac{3N}{2}}\cdot\left(\frac{3N}{2\pi}\right)^{\frac{3N}{2}}$

$\rightarrow$ Komparacijom $\Rightarrow$ $\boxed{C = \left(\frac{2\pi e}{3N}\right)^{\frac{3N}{2}}}$

$$S = K\ln\left[ACV^N(3NmKT)^{\frac{3N}{2}}\right] = K\ln\left[\left(\frac{e}{Nh^3}\cdot\frac{2^{3/2}\pi^{3/2}e^{3/2}}{3^{3/2}N^{3/2}}\cdot V\cdot 3^{3/2}N^{3/2}(mKT)^{3/2}\right)^N\right]$$

$$\Rightarrow \boxed{S = KN\ln\left[\frac{Ve^{5/2}}{N}\left(\frac{2\pi mKT}{h^2}\right)^{3/2}\right]}$$

$\rightarrow$ a to je upravo formula Tetrode sa (36)

Fluktuacije oko srednjih vrijednosti (Kan. ansambla)

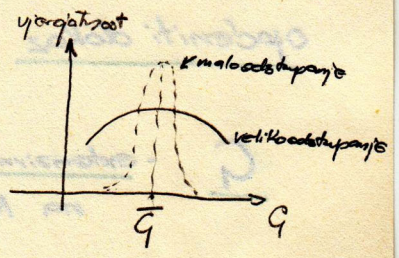
$w = \varrho = A\,\frac{1}{Z}\,e^{-\beta H}$ $\quad F = -\Theta \ln Z \Rightarrow Z = e^{-\beta F}$

$$\bar{G} = \int_\Gamma G\varrho\,d\phi = A\int_\Gamma e^{\beta(F-H)} G\,d\phi = \frac{\int_\Gamma G e^{-\beta H}\,d\phi}{\int_\Gamma e^{-\beta H}\,d\phi}$$

→ treba def. veličinu koja će mjeriti odstupanje od sr. vrij. Kan. ansambla

Standardna devijacija

$$(\Delta G)^2 = \overline{(G-\bar{G})^2}$$ ← usrednji po Kanonskom Kan ansamblu



$$(\Delta G)^2 = \overline{(G^2 - 2G\bar{G} + \bar{G}^2)} = \bar{G}^2 - 2\bar{G}\cdot\bar{G} + \bar{G}^2$$

$$= \bar{G^2} - \bar{G}^2$$

$$\frac{\Delta G}{\bar{G}} = \frac{\sqrt{\bar{G^2} - \bar{G}^2}}{\bar{G}}$$ relativna fluktuacija

$$\sim \frac{1}{\sqrt{N}}$$ očekujemo kod Kan. ansambla

$$1 = A\int_\Gamma e^{\beta(F-H)}\,d\phi \quad /\left(\frac{\partial}{\partial\beta}\right)_V \Rightarrow 0 = A\int_\Gamma e^{\beta(F-H)}\left[\left(\frac{\partial \beta F}{\partial \beta}\right)_V - H\right]d\phi \quad /\left(\frac{\partial}{\partial\beta}\right)_V$$

($\bar{U}$ jer $H(q_1,\dots p_s, V, a')$)

$$0 = A\cdot\left(\frac{\partial \beta F}{\partial \beta}\right)_V \int_\Gamma e^{\beta(F-H)}\,d\phi - A\int_\Gamma H e^{\beta(F-H)}\,d\phi$$

$$\Rightarrow \bar{U} = \bar{H} = \left(\frac{\partial \beta F}{\partial \beta}\right)_V$$

$$0 = A\int_\Gamma e^{\beta(F-H)}\left[\left(\frac{\partial \bar{U}}{\partial\beta}\right)_V - 0 + \left(\left(\frac{\partial \beta F}{\partial\beta}\right)_V - H\right)(\bar{U}-H)\right]d\phi$$

$$0 = A\int_\Gamma \left(\frac{\partial \bar{U}}{\partial\beta}\right)_V e^{\beta(F-H)}\,d\phi + A\int_\Gamma e^{\beta(F-H)}\cdot(H-\bar{U})^2\,d\phi = \overline{(H-\bar{U})^2} = (\Delta H)^2 = (\Delta U)^2$$

$$\Rightarrow \quad (\Delta U)^2 = -\left(\frac{\partial \bar{U}}{\partial\beta}\right)_V$$ $\quad \beta = \frac{1}{\Theta}$

$$C_V = \left(\frac{\partial \bar{U}}{\partial T}\right)_V$$

$\bar{U} = \bar{U}[\beta(T)] \quad \frac{\partial \bar{U}}{\partial \beta} = \frac{\partial \bar{U}}{\partial T}\frac{\partial T}{\partial \beta}$ $\quad \beta = \frac{1}{kT}$ $\quad T = \frac{1}{k\beta}$

$\frac{\partial}{\partial \beta} = -kT^2\frac{\partial}{\partial T}$ $\quad -\frac{1}{k\beta^2} = -\frac{k^2T^2}{k} = -kT^2$

$$\Rightarrow \Delta U = \sqrt{kT^2 C_V}$$

$$\rightarrow \quad \frac{\Delta U}{\bar{U}} = \frac{T\sqrt{kC_v}}{\bar{U}}$$

1-A idealni plin

$$\bar{U} = \tfrac{3}{2}NkT \qquad C_v = \tfrac{3}{2}Nk \quad \Rightarrow \quad \frac{\Delta U}{\bar{U}} = \frac{T\sqrt{\frac{3}{2}Nk^2}}{\frac{3}{2}NkT} = \frac{1}{\sqrt{\frac{3}{2}N}} \sim \frac{1}{\sqrt{N}}$$

opceniti dokaz (bez obzira na Karakter distribucijske fje.) - tj. nemora b.t idealni plin

G - **ekstenzivna** t-dm. fiz. veličina koja pripada sistemu koji se može podijeliti na N podsistema koji **nisu u korelaciji**:

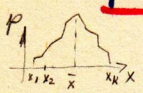
$$\Rightarrow \quad G = \sum_{i=1}^{N} g_i$$

$$\bar{G}^2 = \sum_{i=1}^{N} \overline{g_i^2} + \sum_{\substack{i=1 \\ i\neq j}}^{N}\sum_{j=1}^{N} \overline{g_i g_j} \qquad \bar{G} = \sum_{i=1}^{N} \bar{g}_i$$

$$\bar{G}^2 = \sum_{i=1}^{N} \bar{g}_i^2 + \sum_{\substack{i=1 \\ i\neq j}}^{N}\sum_{j=1}^{N} \bar{g}_i \cdot \bar{g}_j$$

$$\Rightarrow (\Delta G)^2 = \bar{G}^2 - \bar{G}^2 = \sum_{i=1}^{N} \left(\overline{g_i^2} - \bar{g}_i^2 \right) + \sum_{\substack{i=1 \\ i\neq j}}^{N}\sum_{j=1}^{N} \left(\overline{g_i g_j} - \bar{g}_i \bar{g}_j \right)$$

pretp.: ako su podsistemi **nezavisni** (nisu u korelaciji)



→ npr. čestice - podsistemi koje slabo interagiraju (usmisle jedna s drugom, dok ukupna energija inter. 1 čestice sa cijelim sistemom ipak može b.t značajna)

Hinšin - (73)

$$\bar{x} = \sum_{i=1}^{k} x_i p_i \qquad \bar{y} = \sum_{j=1}^{l} y_j p_j$$

$$\overline{xy} = \sum_{i=1}^{k}\sum_{j=1}^{l} (x_i y_j)\, p_{ij}$$

(x_i, y_j) $(k \cdot l)$ parova

$$\Rightarrow \quad \overline{g_i g_j} = \bar{g}_i \cdot \bar{g}_j \quad \text{za } i \neq j$$

$p_{ij}(x_i \,\&\, y_j)$

& ako $p_{ij} = p_i \cdot p_j$ nezav. veličine $\Rightarrow \overline{xy} = \sum_{i=1}^{k} x_i p_i \cdot \sum_{j=1}^{l} y_j p_j = \bar{x}\,\bar{y}$

očit $i = j \Rightarrow$ zavisnost

$$\Rightarrow \quad (\Delta G)^2 = \sum_{i=1}^{N} \left(\overline{g_i^2} - \bar{g}_i^2 \right) = \sum_{i=1}^{N} (\Delta g_i)^2$$

Hinšin - (92)

→ disperzija sume nezavisnih slučajnih veličina jednaka je sumi njihovih disperzija

→ spec.: - ako su podsistemi otvirena termodinamička (čestice)

$G = \sum_{i=1}^{N} g_i \qquad g_i = g \qquad \bar{g}_i = \bar{g} \qquad \Delta g_i = \Delta g \qquad \forall i = 1, \dots N$

$\sqrt{\overline{g_i^2} - \bar{g}_i^2} = \sqrt{\overline{g^2} - \bar{g}^2}$

$\Rightarrow \quad G = N \cdot g \qquad \bar{G} = N \cdot \bar{g} \qquad (\Delta G)^2 = N \cdot (\Delta g)^2$

$$\frac{\Delta G}{\bar{G}} = \frac{\Delta g \sqrt{N}}{\bar{g} \cdot N} = \frac{\Delta g}{\bar{g}} \cdot \frac{1}{\sqrt{N}} \approx \frac{1}{\sqrt{N}}$$

jer Δg & $\bar{g}$ veličine istog reda

→ što je broj nekoreliranih podsistema već. rel. fluktuacija je manja

$\mathcal{H}$ - teorem Boltzmann

$\frac{d\mathcal{H}}{dt} = \frac{\partial \mathcal{H}}{\partial t} = -\frac{\partial \mathcal{L}}{\partial t}$

$\mathcal{H} \overset{def.}{=} \overline{\ln g} = \int_\Gamma g \ln g \, d\phi$

$\ln g \cdot \frac{\partial g}{\partial t} + g \cdot \frac{1}{g} \cdot \frac{\partial g}{\partial t}$

$g = A\, e^{\Theta(F-H)}$ & $H(q_1, \dots p_s, t, a)$ — općenito / vanj. polja; ovisi eksplicitno ovuda ovisi, jedino ne u slučaju t-din. zatvorenog sustava; ravnot. sistema sa termostatom

$\frac{dg}{dt} = 0$ Liouville $\Rightarrow \frac{\partial g}{\partial t} \neq 0$

$$\frac{d\mathcal{H}}{dt} = \int_\Gamma \frac{\partial g}{\partial t} (\ln g + 1)\, d\phi$$

jer $\frac{d\mathcal{H}}{dt} = \frac{\partial \mathcal{H}}{\partial t} + \sum_{i=1}^{s} \left(\dot{q}_i \frac{\partial \mathcal{H}}{\partial q_i} + \dot{p}_i \frac{\partial \mathcal{H}}{\partial p_i} \right)$, pri čemu $\frac{\partial \mathcal{H}}{\partial t} = 0$

jer $\frac{d\mathcal{H}}{dt} = \frac{\partial \mathcal{L}}{\partial t}$

→ ali budući je po $q_1, \dots p_s$ izvršena odred. integracija to $\mathcal{H}$ ne ovisi o njima

→ t-din. ramotežа $H(q_1, \dots p_s, a) = \text{const.}$ $\frac{\partial H}{\partial t} = 0$

$$\frac{\partial g}{\partial t} = 0 \quad \Rightarrow \quad \frac{d\mathcal{H}}{dt} = 0$$

→ općenito - sustav nije u t-din. ravnoteži: $H(q_1, \dots p_s, t, a) \neq \text{const}$ $\frac{\partial H}{\partial t} \neq 0$.
(mijenja mu se svojstvo s vremenom T)

$$\frac{\partial g}{\partial t} \neq 0 \quad \Rightarrow \quad \frac{d\mathcal{H}}{dt} \neq 0$$

da li se povećava ili smanjuje ovisi o konkretnom slučaju

→ pokazuje se $\frac{d\mathcal{H}}{dt} < 0 \quad \Rightarrow \quad \frac{d\mathcal{H}}{dt} \leq 0$

Boltzmann-ov $\mathcal{H}$ - teorem

(teško izreći)

→ Boltzmann-ov izvod -jba. transporta iona u $\vec{E}$

- $\vec{E}$ djeluje kratko vrijeme ⇒ distribuc. fja. ϱ se mijenja
- $\vec{E}$ djeluje stalno ⇒ ϱ se ne mijenja - uspostavilo se stac. stanje

<u>uvjet stacionarnost</u>

⇒ $\mathcal{H}$ teorem

$Z \approx A e^{\beta \bar{u}} \phi(\bar{u})$

$1 = \int_\Gamma \varrho \, d\phi \xrightarrow{\text{aprox.}} 1 = \varrho(\bar{u}) \cdot \phi(\bar{u})$

Opći izvedena (**) na (24.0)

$W \equiv \varrho \quad A = \frac{1}{N! h^s}$ iz $S = -k \left(\frac{\partial \Psi}{\partial \theta}\right)_a$

(*) $S = k \ln A \phi(\bar{u})$

$= k \ln \frac{A}{\varrho(\bar{u})} = k \ln A - k \ln \varrho(\bar{u})$

$S = -k \left(\overline{\ln W} + \ln N! h^s \right)$

$= k \ln A - k \overline{\ln W}$

$\overline{\ln W} = \int \ln W \cdot W(E) dE = \ln W(\bar{u})$

$\bar{G}(H) = G(\bar{u}) \Rightarrow \underline{\ln \varrho(\bar{u}) = \overline{\ln \varrho(H)}}$

$\Rightarrow S = \underbrace{k \ln A}_{\parallel 0} - k \overline{\ln \varrho(H)}$ (**)

jer je ionako redefinirana do na aditivnu konstantu

$$\underline{S = -k \overline{\ln \varrho} = -k \mathcal{H}}$$

$\frac{dS}{dt} \geq 0$ IREV. REV. $\Rightarrow \underline{\frac{d\mathcal{H}}{dt} \leq 0}$

Kao posljedica II stavka t-dinamike

→ Ova razmatranja računata su za idealni sistem - budući je uzeto (*) što je korektno izvedeno samo za idealni plin, tj. opravdana aproksimacija

modifikacija za realne ? ⇒ ne

$PV = NKT \left[1 + B(T) \cdot \frac{N}{V} + C(T) \left(\frac{N}{V}\right)^2 + \ldots \right.$

↑ izrač. preko vrijalnog tm. | razvoj po gustoći

1. Korekcija

Plin jos uvijek dovoljno razrijeđen

1-A

Sile među molekulama centralne ; E_p je sferno simetrična

$$H = \sum_{i=1}^{N} \frac{1}{2m}\left(p_{ix}^2 + p_{iy}^2 + p_{iz}^2\right) + \frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} E_{p_{ij}}(r_{ij})$$

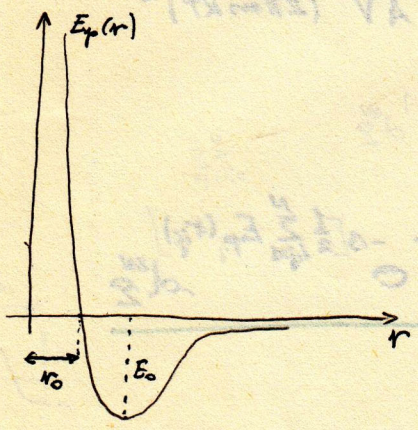
$\frac{1}{2}\sum_{h=1}^{N}\sum_{j=1}^{N} U_{jh}(r_h - r_j)$ $\quad \vec{r}_{jh} = \vec{r}_h - \vec{r}_j$

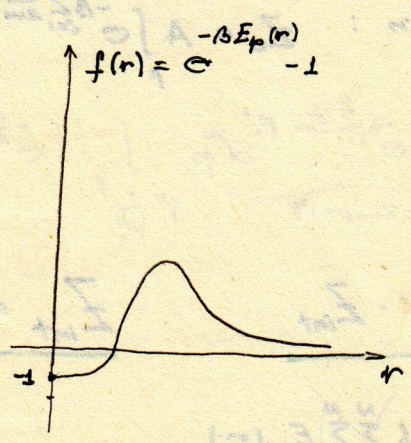
$E_{p_{ii}}(r_{ii}) = 0$ $\quad \vec{r}_{ij} = \vec{r}_i - \vec{r}_j$ druga konvencija

→ opća pretpostavka : nadam egzaktnost fiz. modeli i aprox. radi lakšeg računanja

→ exp. činjenice (za olakšanje i aproksimaciju)

1) Sile - kratkog dosega
2) privlačne sile za $r > r_0$
3) odbojne sile za $r < r_0$





→ analitički prikaz :

$$E_p(r) \simeq \left(\frac{C_1}{r^{12}} - \frac{C_2}{r^6}\right) \qquad C_1, C_2 > 0$$

Lennard - Jones aprox.

dominantno za male udalj. — dominantno za vedeudalj.

$r \to 2r$ $\quad \frac{1}{r^6} \to \frac{1}{r^6}\frac{1}{2^6}$

$\frac{C_1}{r^{12}} - \frac{C_2}{r^6} = 0 \;/\cdot r^{12}$

$C_1 - r^6 C_2 = 0$

$-r^6 C_2 = -C_1$

$r^6 C_2 < C_1$

$r_0 = \sqrt[6]{\frac{C_1}{C_2}}$ $\quad E_p(r_0) = 0$

$E_p(r) > 0 \quad \Rightarrow r < \sqrt[6]{\frac{C_1}{C_2}} = r_0$

Jba. stanja razrijeđenih plinova (realnih)

→ - mala vjerojatnost da unutar dosega interakcije bude više od jedna molekula

1-A ⇒ $E_p(r_{ij})$ sfernosim. fja. $r_{ij} = |\vec{r}_i - \vec{r}_j|$ $|\vec{r}_j - \vec{r}_i|$

$$H = \sum_{i=1}^{N} \frac{1}{2m}\underbrace{(p_{ix}^2 + p_{iy}^2 + p_{iz}^2)}_{p_i^2} + \frac{1}{2}\sum_{\substack{i=1\\ i\neq j}}^{N}\sum_{j=1}^{N} E_{p_{ij}}(r_{ij}) \qquad E_{p_{ii}}(r_{ii}) = 0$$

ili pišemo $\sum_{i=1}^{N}\sum_{j=1}^{N} = \sum_{i,j=1}^{N}$ $(i<j)$ ⇒ samo $E_{p_{12}}$ ane $E_{p_{21}}$ dok $E_{p_{11}} = 0$

$$F = -KT \ln Z$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$Z = A\int_{\Gamma} e^{-\beta H}\, d\phi \qquad A = \frac{1}{N!\,h^{3N}} \qquad d\phi = dq_1 \ldots dq_{3N}\, dp_1 \ldots dp_{3N}$$

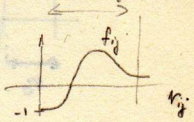
zbog Gibbs-ovog paradoksa

→ za idealan plin: $Z_0 = A\int_{\Gamma} e^{-\beta\sum_{i=1}^{N}\frac{1}{2m}p_i^2} d\phi = A V^N (2\pi m KT)^{\frac{3N}{2}}$

$$Z = \underbrace{A\int_S \cdots \int e^{-\beta\sum_{i=1}^{N}\frac{1}{2m}p_i^2} d^{3N}p}_{A(2\pi m KT)^{\frac{3N}{2}}} \cdot V^N \frac{1}{V^N} \cdot \int_S \cdots \int e^{-\frac{\beta}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} E_{p_{ij}}(r_{ij})} d^{3N}q$$

$\sum_{i=1}^{N}\sum_{j=1}^{N}$

$$\Rightarrow \quad \underline{Z = Z_0 \cdot Z_{int}} \qquad \underline{Z_{int} = \frac{1}{V^N}\int e^{-\beta\left[\frac{1}{2}\sum_{i,j=1}^{N} E_{p_{ij}}(r_{ij})\right]} d^{3N}q}$$



$$\underline{f_{ij} = e^{-\beta\left(\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} E_{p_{ij}}(r_{ij})\right)} - 1}$$

$e^{-\beta E_{p_{ij}}(r_{ij})} = f_{ij} + 1$

$\neq 0$ ako se i-ta & j-ta čestica nalaze u dosegu interakcije

$= 0$ ako i-ta & j-ta čestica dovoljno daleko $\frac{E_p}{KT} \to 0$ za $r \to \infty$, $T \to \infty$ $\Leftarrow$

→ označimo $E_{p_{ij}}(r_{ij}) \equiv E_{ij}$ & $E_{p_{ii}}(r_{ii}) \equiv 0$ tj. $E_{ii} \equiv 0$

popr. (IX) ⇒

$$\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} E_{p_{ij}}(r_{ij}) = \sum^{C_N^2} E_{ij} = \sum_{\substack{i,j\\ i<j}}^{'} E_{ij} = \sum_{j=2}^{N} E_{1j} + \sum_{j=3}^{N} E_{2j} + \ldots + E_{N-1,N}$$

$$Z_{int} = \frac{1}{V^N}\int e^{-\beta\sum_{j=2}^{N} E_{1j}} \cdot e^{-\beta\sum_{j=3}^{N} E_{2j}} \cdots e^{-\beta E_{N-1,N}} d^{3N}q = \frac{1}{V^N}\int \prod_{j=2}^{N}(f_{1j}+1)\prod_{j=3}^{N}(f_{2j}+1)\cdots(f_{N-1,N}+1)\, d^{3N}q$$

$$\overset{!}{=} \frac{1}{V^N}\int \prod_{j=2}^{N}(f_{1j}+1)\, d^3r \cdot \int \prod_{j=1}^{N}(f_{2j}+1)\cdots(f_{N-1,N}+1)\, d^{3(N-1)}q$$

$$\frac{1}{2}\sum_{i=1}^{N}\sum_{j=1}^{N} E_{ij} = \frac{1}{2}\sum^{\overline{V_N^2}} E_{ij}$$

$\overline{V_N^2} = N^2$ člana

sumacija po varijacijama od N elem. 2 reda s ponavlj.

$$\overset{E_{ii}=0}{=} \frac{1}{2}\sum^{V_N^2} E_{ij}$$

sumacija po varijacijama od N elem. 2 reda bez ponavlj.

člana $V_N^2 = N(N-1) = \overline{V_N^2} - N$

$$\overset{E_{ij}=E_{ji}}{=} \frac{1}{2}\cdot 2\cdot\sum^{C_N^2} E_{ij}$$

člana $C_N^2 = \binom{N}{2} = \frac{N(N-1)}{2!} = \frac{V_N^2}{2}$

sumacija po kombinacijama bez ponavljanja

$$\overline{C_N^2} = \binom{N+2-1}{2} = \binom{N+1}{2} = \frac{(N+1)N}{2} = \frac{N(N-1)}{2} + N$$

$$= C_N^2 + N$$

$$= \sum^{C_N^2} E_{ij} \qquad i,j = 1,\dots N$$

$1+2+\dots+(N-1) = \frac{N(N-1)}{2}$

$N-1$ { 12 23 34 ⋯ (N-1)N
13 24 ⋮ 3N
⋮ ⋮
1N 2N

$$= \sum_{j=2}^{N} E_{1j} + \sum_{j=3}^{N} E_{2j} + \dots + E_{N-1N}$$

$$Z_{int} = \frac{1}{V^N}\int \Big(1 + \sum_{j=2}^{N} f_{1j} + \sum_{j,l=2}^{C^2_{N-2}} f_{1j}f_{1l} + \sum_{j,l,k=3}^{C^3_{N-2}} f_{1j}f_{1l}f_{1k} + \dots + \prod_{j=2}^{N}(f_{1j}+1)\Big)\Big(1 + \sum_{j=3}^{N} f_{2j} + \sum_{j,l=2}^{C^2_{N-3}} f_{2j}f_{2l} + \dots + \prod_{j=3}^{N}(f_{2j}+1)\Big)$$

$$\dots\dots\Big(1 + f_{N-1,N}\Big)\, d^{3N}\Omega$$

(*) budući da smo pretp. da je plin razrijeđen, mala je vjerojatnost da u obzir (značajnu interakciju) bude više od jedna molekula, a kamo li više njih → stoga ti viši članovi otpadaju jer barem jedan faktor je sigurno 0.

$$\Rightarrow \quad Z_{int} \approx \frac{1}{V^N}\int \Big(1 + \sum_{j=2}^{N} f_{1j}\Big)\Big(1 + \sum_{j=3}^{N} f_{2j}\Big)\cdots\Big(1 + f_{N-1,N}\Big)\, d^{3N}\Omega$$

zbog (*) na (43) a)

$$Z_{int} \approx \frac{1}{V^N}\int \Big(1 + \sum_{j=2}^{N-1} f_{1j} + \sum_{j=3}^{N-2} f_{2j} + \dots + f_{N-1,N}\Big)\, d^{3N}\Omega = 1 + \frac{N(N-1)}{2V^N}\int f_{ij}\, d^{3N}\Omega$$

$$= 1 + \frac{N(N-1)}{2V^2}\iint f_{ij}\, d^3\vec{r}_i\, d^3\vec{r}_j$$

ili →

$$(*) \Rightarrow \quad Z_{int} = \frac{1}{V^N}\int \Big(1 + \sum_{j=2}^{N} f_{1j}(r_{1j})\Big)\Big(1 + \sum_{j=3}^{N} f_{2j}(r_{2j})\Big)\cdots\Big(1 + f_{N-1,N}(r_{N-1,N})\Big)\, d^3\vec{r}_1\, d^3\vec{r}_2 \cdots d^3\vec{r}_N$$

$$= \frac{1}{V^N}\int \Big(1 + \sum_{j=2}^{N} f_{1j}(r_{1j})\Big) d^3\vec{r}_1 \cdot \int \Big(1 + \sum_{j=3}^{N} f_{2j}(r_{2j})\Big) d^3\vec{r}_2 \cdots \iint \Big(1 + f_{N-1,N}(r_{N-1,N})\Big) d^3\vec{r}_{N-1}\, d^3\vec{r}_N$$

za $\vec{u} = \frac{\vec{r}_N + \vec{r}_{N-1}}{2}$, $\vec{r}_{N-1,N} = \vec{r}_N - \vec{r}_{N-1}$

$$= \frac{1}{V^N}\int \Big(1 + \sum_{j=2}^{N} f_{1j}(r_{1j})\Big) d^3\vec{r}_1 \cdot \int \Big(1 + \sum_{j=3}^{N} f_{2j}(r_{2j})\Big) d^3\vec{r}_2 \cdots \int \Big(1 + f_{N-1,N}(r_{N-1,N})\Big) d^3\vec{r}_{N-1,N} \int d^3\vec{u}$$

$$I_s = \int \Big(1 + \sum_{j=s+1}^{N} f_{sj}(r_{sj})\Big) d^3\vec{r}_s \qquad s = 1, 2, \dots N-2$$

gdje $f_{NN}(r_{NN}) \equiv 0$, $e^{-\beta E_p(r_{NN})} - 1 = 0$

$$I_N = \int d^3\vec{u} = V = \Big[V + (N-N)\int f(r) d^3r\Big]$$

$$I_{N-1} = \int \Big(1 + f_{N-1,N}(r_{N-1,N})\Big) d^3\vec{r}_{N-1,N} = \Big[V + \int f_{N-1,N}(r_{N-1,N}) d^3\vec{r}_{N-1,N}\Big] = \Big[V + (N-(N-1))\int f(r) d^3r\Big]$$

$$I_s = V + \sum_{j=s+1}^{N}\int f_{sj}(r_{sj})\, d^3\vec{r}_s \qquad s = 1, \dots (N-2)$$

originalno!!! budući je svaki uvjet $j \neq s$ jer $j = s+1, \dots N$ to $\vec{r}_{sj} = \vec{r}_j - \vec{r}_s$ možemo zamisliti da sve te $\vec{r}_j$ držimo stalnim pri svim mogućim promjenama $\vec{r}_s$ ⇒ ⇒ $\vec{r}_{sj}$ prolazi kroz svemoguće vrijednosti

$$\Rightarrow \int f_{sj}(r_{sj}) d^3\vec{r}_s = \int f_{sj}(r_{sj}) d^3\vec{r}_{sj} = 2\pi\int_0^\infty r_{sj}^2 f_{sj}(r_{sj}) dr_{sj} = 2\pi\int_0^\infty r^2 f(r) dr = \int f(r) d^3r$$

$$\Rightarrow I_s = \Big[V + (N-s)\int f(r) d^3r\Big] = \Big[V + (N-s)\cdot\int\Big(e^{-\beta E_p(r)} - 1\Big) d^3r\Big]$$

$$I_s = \big[V - 2B(N-s)\big] \qquad s = 1, \dots N-2 \qquad 2B(T) = \int \big(1 - e^{-\beta E_p(r)}\big) d^3r$$

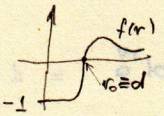
$$\Rightarrow Z_{int} = \frac{1}{V^N} \prod_{s=1}^{N} [V - 2B(N-s)] \qquad 2B(T) = -\int f(r)\, d^3r = \int (1 - e^{-\beta E_p(r)})\, d^3r$$

$$= \prod_{s=1}^{N} \left[1 - 2B\,\frac{N-s}{V}\right]$$

uz pretp. (*) tj. dovoljno razrijeđenom realnom plinu

$$Z = Z_0 \cdot Z_{int} = AV^N (2\pi m k T)^{\frac{3N}{2}} \cdot \prod_{s=1}^{N} \left[1 - 2B(T)\,\frac{N-s}{V}\right]$$

$E_0 \ll kT \Rightarrow \alpha f_{ij}(r_{ij}) \ll 1$



(43a) *) $\Rightarrow$ $|f(r)| \ll 1$ $r > r_0$; $|f(r)| \leq 1$ $r \leq r_0$ } (**) i.e. $R \gg r_0$

originalno !!:

$$|2B(T)| = \left| -\int f(r)\, d^3r \right| = \left| -4\pi \int_0^{\infty R} r^2 f(r)\, dr \right| \leq 4\pi \int_0^{\infty R} r^2 |f(r)|\, dr \ll 4\pi \int_0^{\infty R} r^2\, dr = V$$

& (**) na (44)

bitno $\rightarrow$ R - polumjer posude $V = \frac{4}{3}R^3\pi$

jer $f(\infty) = f(R) = 0$

oprovdana pretp.: $V \gg 2B(T)(N-1) \Rightarrow V \gg 2B(N-s)$ $s = 1, \ldots N$

$$x_s = \frac{2B(T)(N-s)}{V} \ll 1 \qquad s = 1, \ldots N$$

$$F = -kT \ln Z = -kT \ln Z_0 - kT \ln Z_{int} = F_0 + F_{int}$$

$$F_{int} = -kT \ln Z_{int} = -kT \ln \prod_{s=1}^{N} \left[1 - 2B\,\frac{N-s}{V}\right]$$

$x_s \ll 1 \Rightarrow \ln(1 - x_s) \approx x_s$

$\ln(1-x) = -x - \frac{x^2}{2} - \frac{x^3}{3} - \ldots$

$$= -kT \left[\sum_{s=1}^{N} \ln\left(1 - \frac{2B(T)(N-s)}{V}\right)\right] = -kT \left[\sum_{s=1}^{N} \ln(1 - x_s)\right] \approx -kT \sum_{s=1}^{N} -x_s$$

$$= kT \cdot \frac{2B(T)}{V} \sum_{s=1}^{N} (N-s) \qquad \frac{(N-1)(N-1+1)}{2}$$

!!! odmah gore

$$= kT \cdot \frac{2B(T)}{V} \cdot \frac{N(N-1)}{2} \overset{N \gg 1}{=} kT\,\frac{B(T) \cdot N^2}{V}$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = -\left(\frac{\partial F_0}{\partial V}\right)_T - \left(\frac{\partial F_{int}}{\partial V}\right)_T = \underbrace{P_0}_{\frac{NkT}{V}} + kT\,\frac{B(T)\,N^2}{V^2}$$

$$\Rightarrow \quad P = \frac{NkT}{V}\left[1 + B(T) \cdot \frac{N}{V}\right]$$

$\frac{N}{V}$ gustoća plina

B virijalni koef.

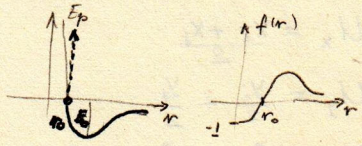
(43) a)

$$Z_{int} = \frac{1}{V^N}\int_{3N}\prod_{i=2}^{N}(f_{1i}+1)\prod_{j=2}^{N}(f_{2j}+1)\cdots(f_{N-1,N}+1)\,d^{3N}\vec{r} = \frac{1}{V^N}\int_{3N}\prod_{i\neq j}^{N}(1+f_{ij})\,d^{3N}\vec{r}$$

$\prod_{i\neq j}^{N} = \prod_{i<j}^{C_N^2}$

$$Z_{int} = \frac{1}{V^N}\int_{3N}\cdots\int\underbrace{\prod_{j=2}^{N}(1+f_{1j})\prod_{j=3}^{N}(1+f_{2j})\cdots(1+f_{N-1,N})}_{\prod_{i<j}^{C_N^2}(1+f_{ij})}\,d^3\vec{r}_1\cdots d^3\vec{r}_N$$

$$f_{ij}(r_{ij}) = e^{-\beta E_p(r_{ij})} - 1$$



$|E_{p\,min}| = E_0 > 0$

➡ **interakcija među molekulama slaba** ⇔ **razrijeđen realni plin** ⇒

⇒ mala vjerojatnost da unutar dosega interakc. bude više od jedna molek.

➡ (*) $E_0 \ll KT$

ukvantnoj se pokazuje da ovo nije tako jako

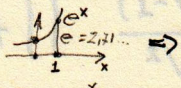
⇒ za $r > r_0$ $E_p < 0 \Rightarrow x > 0$

$$x_{max} = (-\beta E_{p\,min})_{max} = \left(-\frac{E_p}{KT}\right)_{max} = -\frac{E_{p\,min}}{KT} = \frac{E_0}{KT} \ll 1$$

& $x = -\beta E_p(r) > 0$, $x < x_{max}$

tj. pot. energija interakcije po molekuli je mnogo manja od energije translatornog gibanja (koja je reda veličine KT)

$\Rightarrow 0 < x \ll 1$



$\Rightarrow f(r) = e^x - 1 \ll 1$ *)

$\Rightarrow e^x \ll 2 \quad e^x - 1 \ll 1$

ili → za $x \ll 1$ $f(r) = \left(1 + \frac{x}{1!} + \frac{x^2}{2!} + \cdots\right) - 1 \approx x = -\frac{E_p}{KT} \ll 1$

$\Rightarrow f(r) \ll 1$

$\Rightarrow 0 < f_{ij}(r_{ij}) \ll 1$ za $\forall i \neq j$ *) (bolje za $\forall C_N^2$)

→ elementa f_{ij} ima C_N^2 $\binom{C_N^2}{2}$ parova - kombinacije bez ponavljanja od C_N^2 atom 2-razreda $\binom{C_N^2}{C_N^2} = 1$

$$\prod_{i<j}^{C_N^2}(1+f_{ij}) = 1 + \sum_{i<j}^{C_N^2}\sum_{k<l}^{C_N^2} f_{ij}\cdot f_{kl} + \sum_{i<j}^{C_N^2} f_{ij} + \cdots + \prod_{i<j}^{C_N^2} f_{ij} \approx$$

($\sum\sum \approx 0$)

$$\approx 1 + \sum_{i<j}^{C_N^2} f_{ij}$$

oznaka da suma ide po kombinacijama bez ponavljanja

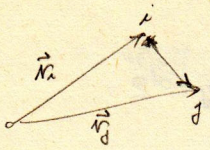
$$Z_{int} = \frac{1}{V^N}\int_{3N}\cdots\int\left(1 + \sum_{i<j}^{C_N^2} f_{ij}(|\vec{r}_j - \vec{r}_i|)\right)d^3\vec{r}_1\cdots d^3\vec{r}_N \qquad f_{ij}(r_{ij}) \quad \vec{r}_{ij} = \vec{r}_j - \vec{r}_i$$

$$= \frac{1}{V^N}\int_{3N}\cdots\int d^3\vec{r}_1\cdots d^3\vec{r}_N + \frac{1}{V^N}\sum_{i<j}^{C_N^2 = \binom{N}{2}}\underbrace{\int_{3N}\cdots\int f_{ij}(|\vec{r}_j - \vec{r}_i|)\,d^3\vec{r}_1\cdots d^3\vec{r}_N}_{V^{N-2}\cdot\iint f_{ij}(|\vec{r}_j - \vec{r}_i|)\,d^3\vec{r}_i\,d^3\vec{r}_j}$$

$$= 1 + \sum_{i<j}^{C_N^2}\frac{1}{V^2}\iint f_{ij}(|\vec{r}_j - \vec{r}_i|)\,d^3\vec{r}_i\,d^3\vec{r}_j$$

Svi ovi integrali međusobno isti.

$$= 1 + \frac{N(N-1)}{2V^2}\iint f_{ij}(|\vec{r}_j - \vec{r}_i|)\,d^3\vec{r}_i\,d^3\vec{r}_j$$



$\vec{r}_{ij} = \vec{r}_j - \vec{r}_i$ $\quad \vec{R} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{m_1+m_2}$ $\quad \vec{r} = \vec{r}_{ab} = \vec{r}_a - \vec{r}_b$

$$\vec{U} = \frac{\vec{r}_i + \vec{r}_j}{2} \qquad \vec{r}_{ij} = \vec{r}_j - \vec{r}_i = \vec{r}$$

$d^3\vec{r}_i \, d^3\vec{r}_j \qquad d^3\vec{r} \; d^3\vec{u}$

$dx_i \dots dz_j = \left|\frac{\partial(x_i, \dots z_j)}{\partial(x_1, \dots u_z)}\right| dx \dots du_z$

$$U_x = \frac{x_i + x_j}{2} \qquad x = x_j - x_i$$
$$U_y = \frac{y_i}{2} + \frac{y_j}{2} \qquad y = y_j - y_i$$
$$U_z = \frac{z_i}{2} + \frac{z_j}{2} \qquad z = z_j - z_i$$

$$\Rightarrow \frac{\partial(x_j \dots u_z)}{\partial(x_i, \dots z_j)} = \begin{vmatrix} -1 & 0 & 0 & \frac{1}{2} & 0 & 0 \\ 0 & -1 & 0 & 0 & \frac{1}{2} & 0 \\ 0 & 0 & -1 & 0 & 0 & \frac{1}{2} \\ 1 & 0 & 0 & \frac{1}{2} & 0 & 0 \\ 0 & 1 & 0 & 0 & \frac{1}{2} & 0 \\ 0 & 0 & 1 & 0 & 0 & \frac{1}{2} \end{vmatrix} = -1$$

$$\Rightarrow \quad d^3\vec{r}_i \, d^3\vec{r}_j = d^3\vec{r}_{ij} \, d^3\vec{u}$$

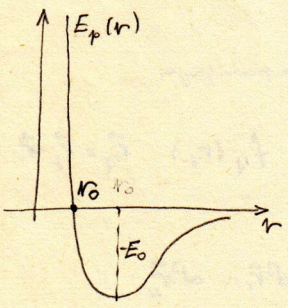
$$Z_{int.} = 1 + \frac{N(N-1)}{2V^2} \iint f_{ij}(r_{ij}) \, d^3\vec{r}_{ij} \, d^3\vec{u}$$

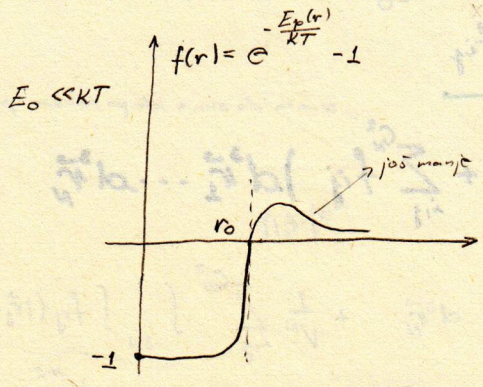
$$= 1 + \frac{N(N-1)}{2V} \int f_{ij}(r_{ij}) \, d^3\vec{r}_{ij} \qquad = 4\pi \int_0^\infty f_{ij}(r) \cdot r^2 dr$$

$N \gg 1 \Rightarrow N(N-1) \approx N^2$

$$= 1 + \frac{2\pi N^2}{V} \int_0^\infty r^2 f(r) dr$$

$$Z_{int} = 1 + \frac{2\pi N^2}{V} \left[\int_0^{r_0} r^2 f(r) dr + \int_{r_0}^\infty r^2 f(r) dr \right]$$





$r < r_0 \quad f(r) \approx -1$

(*) & $r > r_0 \quad f(r) \approx -\frac{E_p(r)}{kT}$

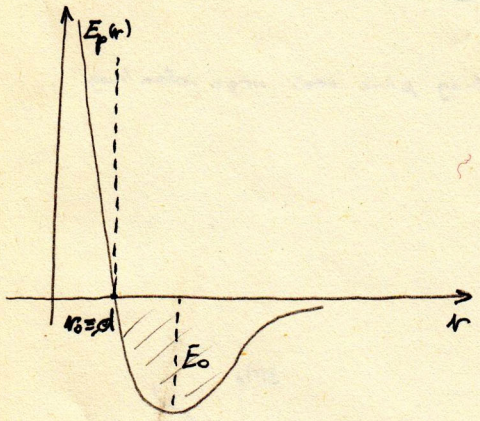
$f(r) = e^x - 1 \qquad x = -\frac{E_p(r)}{kT} \ll 1$

$\approx \frac{x}{1!}$ za $r > r_0$ jer dovoljno $x > 0$

$$Z_{int} = 1 - \frac{N^2}{V} \left[\frac{2\pi \cdot r_0^3}{3} + \frac{2\pi}{kT} \int_{r_0}^\infty r^2 E_p(r) dr \right]$$

Idealizacija:

$f(r) = e^{-\beta E_p(r)} - 1$



$E_p(r) = \infty \quad r \le d$

$E_p(r) < 0 \quad r > d \qquad E_p(r) \approx -\frac{C_1}{r^6}$

$E_p(r) \simeq \frac{C_1}{r^{12}} - \frac{C_2}{r^6} \qquad C_1, C_2 > 0$ (dominira zadnja veličina)

$2B(T) = -\int f(r)\, d^3r = \int (1 - e^{-\beta E_p(r)})\, d^3r$

$E_p(d) = 0 \Rightarrow r_0 = d = \sqrt[6]{\frac{C_1}{C_2}}$

$E_{p\,min.}$ za $r_{min} = \sqrt[6]{\frac{2C_1}{C_2}} = \sqrt[6]{2}\cdot d$

$-E_0 = \frac{C_1}{\left(\frac{2C_1}{C_2}\right)^2} - \frac{C_2}{\frac{2C_1}{C_2}}$

$E_0 = \frac{C_2^2}{4C_1} = \frac{C_2}{4d^6}$

$C_2 = 4d^6 E_0$

$C_1 = 4d^{12} E_0$

$$B(T) = \frac{1}{2}\int (1 - e^{-\beta E_p(r)})\, d^3r = \frac{1}{2}\cdot 4\pi \int_0^\infty (1 - e^{-\beta E_p(r)})\, r^2 dr$$

$$= 2\pi \int_0^d r^2 dr - 2\pi \int_d^\infty (e^{-\beta E_p(r)} - 1)\, r^2 dr$$

$$= 2\pi \frac{d^3}{3} - \frac{a}{kT} = \underline{b - \frac{a}{kT}}$$

$b = \frac{2\pi d^3}{3} > 0$

$d \sim$ lin. dimenzija molekule

$b \simeq$ volumena 1 molekule

$a = 2\pi kT \int_d^\infty (e^{-\frac{E_p(r)}{kT}} - 1)\, r^2 dr > 0$

jer za $r > d$: $E_p(r) < 0 \Rightarrow e^{-\frac{E_p(r)}{kT}} > 1$

$\Rightarrow B(T) = b - \frac{a}{kT} <$ vol. 1 molek. $\ll \frac{V}{N-1}$ **)

→ procjena a ⇒ da li je $B(T)$ poz. ili neg. ⇒ tj. da li kod realnog plina P veći ili manji nego kod istog idealnog

($x \to 1$) $E_0 \ll kT$ visoke temp.

$e^x = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \dots$

$\Rightarrow e^{-\frac{E_p}{kT}} \overset{r>d}{=} e^{\frac{|E_p|}{kT}} \overset{|E_p| \le E_0}{\approx} 1 - \frac{E_p}{kT}$ ili $1 + \frac{|E_p|}{kT}$

$\Rightarrow e^{-\frac{E_p}{kT}} - 1 \approx -\frac{E_p}{kT}$

$$a = -2\pi \int_d^\infty r^2 E_p(r)\, dr \approx -2\pi \int_d^\infty r^2 \cdot \left(-\frac{C_2}{r^6}\right) dr = 2\pi C_1 \int_d^\infty r^{-4} dr = \frac{2\pi C_2}{-4+1}\left(\frac{1}{r^3}\right)$$

$$\approx -\frac{2\pi C_2}{3}\cdot\left(\frac{1}{\infty} - \frac{1}{d^3}\right) = \frac{2\pi C_2}{3d^3} = \frac{8\pi}{3} E_0 d^3$$

Lennard-Jones ⇒ $a \approx \frac{2\pi C_2}{3d^3} - \frac{2\pi C_1}{9d^9} = \frac{8\pi E_0 d^6}{3d^3} - \frac{8\pi E_0 d^{12}}{9d^9} = \frac{16\pi}{9} E_0 d^3$

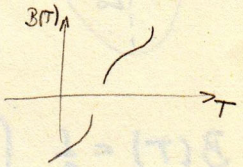
⇒ za veliko T a praktički ne ovisi o T

$$B(T) = b - \frac{a}{KT} \approx \frac{2\pi d^3}{3} - \frac{16\pi d^3}{9} \cdot \frac{E_0}{KT} \quad \left(\frac{E_0}{KT} \ll 1\right)$$

$\Rightarrow$ $B(T) \approx b > 0$ $\Rightarrow$ tlak realnog plina veći nego idealnog

2) $E_0 \gg KT$ niže temp.

$$a = 2\pi KT \int_d^\infty \left(e^{\frac{|E_p(r)|}{KT}} - 1 \right) r^2 dr$$



$B(T) = b - \frac{a}{KT}$ na niskim temp. $B < 0$

→ **def:** $B(T_B) = 0$ T_B - Boyl-ova temp.

$\Rightarrow$ $PV = NKT$ za $T \approx T_B$

→ usporedba s Waals-der Waals-ovom jbom:

$$P = \frac{NKT}{V}\left[1 + \frac{N}{V}\left(b - \frac{a}{KT}\right)\right]$$

$$\left(P + a\frac{N^2}{V^2}\right)(V - Nb) = NKT \quad (**)$$

$n = \frac{N}{\tilde{N}}$ $R = \tilde{N}K$

$\left(P + \frac{a'}{V^2}\right)(V - b') = RT$ $V = \frac{V}{n}$

$V = \frac{V \cdot \tilde{N}}{N}$

$\left(P + a'\frac{N^2}{V^2 \tilde{N}^2}\right)\left(\frac{V \cdot \tilde{N}}{N} - b'\right) = \tilde{N}KT \quad / \cdot \frac{N}{\tilde{N}}$

$\left(P + \underbrace{\frac{a'}{\tilde{N}^2}}_{a} \cdot \frac{N^2}{V^2}\right) \cdot \left(V - N \cdot \underbrace{\frac{b'}{\tilde{N}}}_{b}\right) = NKT$ ←

$$P = \frac{NKT}{V - Nb} - a\frac{N^2}{V^2} = \frac{NKT}{V}\left[1 + \frac{Nb}{V} + \left(\frac{Nb}{V}\right)^2 + \dots - \frac{aN}{VKT}\right]$$

$\frac{1}{1 - \frac{Nb}{V}}$

b - volum. 1 molek. $\Rightarrow \frac{Nb}{V} \ll 1$ (**) za dosta razrjed. plin.

$$P = \frac{NKT}{V}\left[1 + \frac{N}{V}\left(b - \frac{a}{KT}\right)\right] + \frac{NKT}{V}\left[b^2\frac{N^2}{V^2} + \dots\right]$$

$\Rightarrow$ slaganje s lin. članom u razvoju

3. virij. koef. se ne podudara sa $b^2\frac{N^2}{V^2}$ dalko dobro

Neslaganja teor. s exp. rezultatima

1) Gibbs-ov paradox $A \sim \frac{1}{N!}$ inače ne vrijedi adit. entrop.

- protp. da jednake čestice možemo razlikovati:
  $\Delta p \cdot \Delta q \gtrsim h$

- taj nedostatak klas. stat. fizike ne ovisi o T

2) temp. ovisni nedostaci:

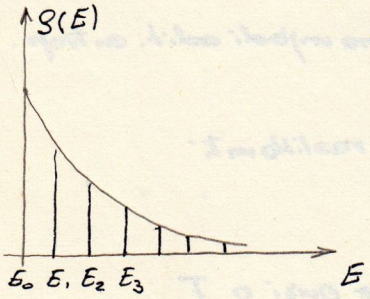
Niske temp.

- H_2 za $T \lesssim 80°K$ ponaša se kao 1-A → zamrzav. rotac. st. slobode
- Kristalna rešetka $C_v = \text{const.}$ - u skladu s exp. na visokim temp., ali u supr. sa exp. na niskim temp.
  $C_v \sim \frac{1}{T^3}$ u blizini apsol. nule
- elektroni u metalima trebali bi dati svoj doprinos ukupnom kapacitetu C_v metala, a ne daju → zamrznuti stupnjevi
- Jeans - Rayleigh zakon $u_\omega \sim \omega^2$ za $\omega \gg$ $u_\omega \sim \omega^3 e^{-\alpha\omega}$ exp.
  vrijedi za male ω
  za $\hbar\omega \gg kT$ vodi do pogrš. rezultata i odstupa od exp. spektr. fje

C_v - konačno u suprotnosti sa III z.t.d.
$\lim_{T\to 0} C_v \to 0$

→ Kvantizacija energije objašnjava sve te nedostatke i III z.t.d.

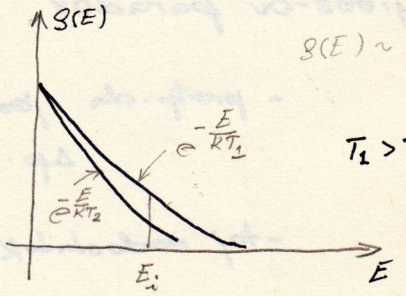
Termička pobuđenja na niskim temp.



Boltzmann. rasp.

$$g(E) \sim e^{-\frac{E}{KT}}$$

→ daje omjeru pobuđenih stanja



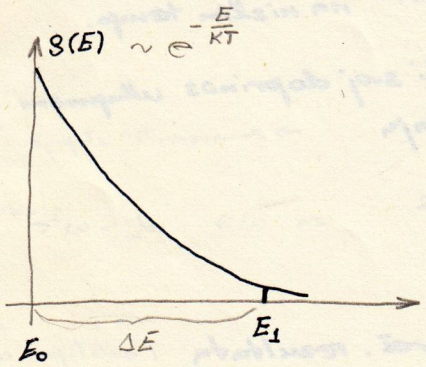
energetski diskontinuum

→ interes čestica prema višim stanjima manji

na niZim temp. pobuđenost viših energ. stanja slabija

→ uvedimo

Kvantizacija energija



→ prvo pobuđeno se nalazi dovoljno daleko (visoko) od osnovnog

⇒ na E_1 može prijeći samo mali broj čestica

drastična promjena u razmaku

→ prema Boltzmannu - stupanj termičkog pobuđenja sistema vrlo mali

$E_1 - E_0 = \Delta E$

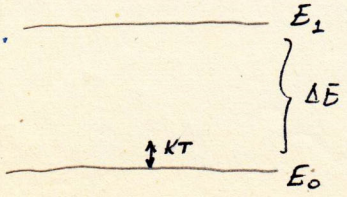
$$\frac{g(E_1)}{g(E_0)} \sim e^{-\frac{(E_1 - E_0)}{KT}} = e^{-\frac{\Delta E}{KT}}$$

$\frac{\Delta E}{KT} \gg 1$

Za $\Delta E \gg KT$ niske temp. $g(E_1) = \frac{g(E_1)}{g(E_0)} \sim e^{-\frac{\Delta E}{KT}} \to 0$

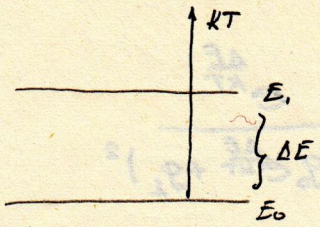
→ termičko pobuđenje jedva da djeluje na promatrani sistem

→ sistem ne preuzima energiju (toplinu) ⇒ $C_V \to 0$



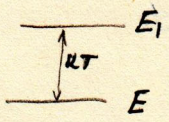
→ Kvantna statistika

za $\Delta E \ll KT$



- Kvantizacija energ. nema vel. značenja, jer su gusto poređ. kvantna stanja
- uz izvjesne korekcije ima Klas. statistika

za $E_1 - E_0 = KT$



$S, C_v = ?$

$$\bar{E} = \frac{\int E e^{-\beta E} d\phi}{\int e^{-\beta E} d\phi}$$

Klasična statistika

$$\bar{E} = \frac{\sum_i E_i g_i e^{-\beta E_i}}{\sum_i g_i e^{-\beta E_i}}$$

Kvantizacija energije

i-ti energ. nivo

$\beta = \frac{1}{KT}$

g_i - broj mogućih stanja iste energ. E_i

Particiona fja (suma stanja)

$$Z = \sum_i g_i e^{-\beta E_i} \Rightarrow \bar{E} = -\frac{d}{d\beta} \ln Z$$

Model dvaju energetskih nivoa

i) $Z = g_0 e^{-\beta E_0} + g_1 e^{-\beta E_1} = e^{-\beta E_0}\left(g_0 + g_1 e^{-\beta(E_1 - E_0)}\right)$

ii) $f = -KT \ln Z = E_0 - KT \ln\left(g_0 + g_1 e^{-\frac{\Delta E}{KT}}\right)$

iii) $S = -\left(\frac{df}{dT}\right)_V = K\left[\ln\left(g_0 + g_1 e^{-\frac{\Delta E}{KT}}\right) + \frac{g_1 \cdot \frac{\Delta E}{KT}}{g_0 e^{\frac{\Delta E}{KT}} + g_1}\right] = \frac{\bar{E} - f}{T}$

iv) $\bar{E} = E_0 + \frac{g_1 \Delta E}{g_0 e^{\frac{\Delta E}{KT}} + g_1}$

$$\bar{E} = \frac{g_0 E_0 e^{-\beta E_0} + g_1 E_1 e^{-\beta E_1}}{g_0 e^{-\beta E_0} + g_1 e^{-\beta E_1}} = \frac{e^{-\beta E_1}\left(g_0 E_0 e^{+\beta \Delta E} + g_1 (E_0 + \Delta E)\right)}{e^{-\beta E_1}\left(g_0 e^{+\beta \Delta E} + g_1\right)}$$

$$\bar{E} = E_0 + \frac{g_1 \Delta E}{g_0 e^{\frac{\Delta E}{KT}} + g_1} \qquad g_1 \Delta E \cdot \frac{-g_0 e^{\frac{\Delta E}{KT}} \left(-\frac{\Delta E}{KT^2}\right)}{(\quad)^2}$$

$$\frac{d\bar{E}}{dT} = K g_0 g_1 \left(\frac{\Delta E}{KT}\right)^2 \cdot \frac{e^{\frac{\Delta E}{KT}}}{\left(g_0 e^{\frac{\Delta E}{KT}} + g_1\right)^2}$$

1) $\Delta E \gg KT$ niske temp. $\Rightarrow g_0 e^{\frac{\Delta E}{KT}} \gg g_1$

$$\Rightarrow \frac{d\bar{E}}{dT} = K \frac{g_0}{g_1} \left(\frac{\Delta E}{KT}\right)^2 e^{-\frac{\Delta E}{KT}} \to 0 \quad \text{za } T \to 0$$

→ slaganje s III z.t.d.

što je T manji to pravi broj energ. nivoa praktički odrezan

-> kao za molekule rot. sh. slobode praktički zamrznute, a translacioni koji su gusti jos djeluju

H_2 $T = 80°K$

$\lim_{T\to 0} S = K \ln g_0$ ranije opć. prema Boltzmanu $S = K \ln B$

t-dim. vjerojatnost nekog makroskop. stanja

→ g_0 t-dim. vjerojatnost ~ broju različitih ćelija na E_0

→ $g_0 = 1$ tj. ako je najniže energ. stanje nedegenerirano

$\Rightarrow S = K \ln 1 = 0$

općenito više stanja na E_0 $\Rightarrow S \neq 0$ za $T \to 0$

Model dvaju energ. nivoa

→ u klas. fiz. stat. prosjek

$$\bar{G} = \frac{\int G\, e^{-\frac{H}{kT}} d\phi}{\int e^{-\frac{H}{kT}} d\phi}$$

H - hamilt. plina

→ kod Bolt. raspr. sve sa diskr. nivoa prešli na kontinuirane

$$\bar{G} = \frac{\sum_i g_i G_i e^{-\frac{E_i}{kT}}}{\sum_i g_i e^{-\frac{E_i}{kT}}}$$

rezultat kvantne stat. fizike

$$Z = \sum_i g_i e^{-\beta E_i}$$ particij. fja. 1 čestice

$$\bar{E} = \frac{\sum_i g_i E_i e^{-\beta E_i}}{\sum_i g_i e^{-\beta E_i}} = -\frac{d}{d\beta} \ln Z \qquad \beta = \frac{1}{kT}$$

isti oblik kao u klas. stat. fizici

→ sistem koji se nalazi u stanju E_0 & E_1

E_1, g_1

E_0, g_0

sve što ćemo govoriti možemo primijeniti i na slučajeve za veći broj energ. nivoa, jako je temp niska pa dolazi do prijelaza 0-1 1-2 2-3 itd. itj. nema preskakanja nivoa

$E, C_v, S = ?$

$$Z = g_0 e^{-\beta E_0} + g_1 e^{-\beta E_1} = e^{-\beta E_0}\left(g_0 + g_1 e^{-\beta \Delta E}\right) \qquad \Delta E = E_1 - E_0$$

$-\beta E_1 - (-\beta E_0) = -\beta E_1 + \beta E_0 = \beta(E_0 - E_1) = -\beta(E_1 - E_0)$

slob. energ. 1 čestice:

$$f = -kT \ln Z = -kT\left[-\frac{E_0}{kT} + \ln\left(g_0 + g_1 e^{-\beta \Delta E}\right)\right]$$

$$f = E_0 - kT \ln\left(g_0 + g_1 e^{-\beta \Delta E}\right)$$

$$\bar{E} = \frac{g_0 E_0 e^{-\beta E_0} + g_1 E_1 e^{-\beta E_1}}{g_0 e^{-\beta E_0} + g_1 e^{-\beta E_1}} = E_0 + \frac{g_1 \Delta E}{g_0 e^{\frac{\Delta E}{kT}} + g_1}$$

$E_0 + \Delta E$

$-\beta(E_0 - E_1)$

$$= \frac{g_0 E_0 e^{+\beta \Delta E} + g_1 E_1}{g_0 e^{\beta \Delta E} + g_1} = \frac{g_0 E_0 e^{\beta \Delta E} + g_1 E_0 + g_1 \Delta E}{g_0 e^{\beta \Delta E} + g_1}$$

$f = \bar{E} - S \cdot T$ — S - entropija 1 čestice

$$S = \frac{\bar{E} - f}{T} = k \ln\left(g_0 + g_1 e^{-\beta \Delta E}\right) + \frac{g_1 \Delta E}{T\left(g_0 e^{\frac{\Delta E}{kT}} + g_1\right)}$$

Topl. kapacitet 1 čestice:

$$\frac{d}{dT}\left(\frac{g_1 \Delta E}{g_0 e^{\frac{\Delta E}{kT}} + g_1}\right) = g_1 \Delta E \cdot \frac{-1 \cdot \frac{\Delta E}{k} \cdot g_0 e^{\frac{\Delta E}{kT}} \cdot \left(-\frac{1}{T^2}\right)}{\left(g_0 e^{\frac{\Delta E}{kT}} + g_1\right)^2}$$

$$\frac{d\bar{E}}{dT} = k g_0 g_1 \left(\frac{\Delta E}{kT}\right)^2 \frac{e^{\frac{\Delta E}{kT}}}{\left(g_0 e^{\frac{\Delta E}{kT}} + g_1\right)^2}$$

a) jako visoke T $\quad kT \gg \Delta E$

$$\lim_{T \to \infty} S = k \ln(g_0 + g_1)$$

$S = k \ln B$ — spec. oblik Boltz. relacije

- nema razlike između energ. nivoa tj. čestice lako prelaze sa jednog nivoa na drugi; podmaka je vjerojatnost pobuđenja osnovnog i prvog stanja
- broj različitih kvant. stanja koja čestica može zauzeti je $g_0 + g_1$ i to je t-din. vjerojatnost

$$\bar{E} = \frac{E_0 g_0 + E_1 g_1}{g_0 + g_1} = \frac{g_0 g_1}{(g_0 + g_1)^2} \cdot \frac{(\Delta E)^2}{kT}$$

$$\bar{E} = E_0 + \frac{g_1 \Delta E}{g_0 e^{\frac{\Delta E}{kT}} + g_1}$$

$\frac{\Delta E}{kT} \ll 1$

$e^{\frac{\Delta E}{kT}} \approx 1 + \frac{\Delta E}{kT}$

$$\bar{E} = E_0 + \frac{g_1 \Delta E}{g_0 + g_1 + g_0 \frac{\Delta E}{kT}}$$

$x \ll 1$

$\frac{1}{1+x} \approx 1 - x + x^2$

$$\bar{E} = E_0 + \frac{g_1 \Delta E}{g_0 + g_1} \cdot \frac{1}{1 + \frac{g_0}{g_0 + g_1} \frac{\Delta E}{kT}}$$

$\frac{g_0}{g_0 + g_1} < 1$

$$\bar{E} = E_0 + \frac{g_1 \Delta E}{g_0 + g_1}\left[1 - \frac{g_0}{g_0 + g_1} \cdot \frac{\Delta E}{kT}\right]$$

$$\bar{E} = \frac{E_0 g_0 + E_1 g_1}{g_0 + g_1} - \frac{g_0 g_1}{(g_0 + g_1)^2} \cdot \frac{(\Delta E)^2}{kT}$$

$\bar{E} \approx \frac{E_0 g_0 + E_1 g_1}{g_0 + g_1}$

$\Rightarrow$ g_0, g_1 su stat. vjeroj. 0 & 1 nivoa

b) jako niske T $\quad kT \ll \Delta E$

tada su slabo vjerojatna term. pobudenja sustava

$$\bar{E} = E_0 + \frac{g_1}{g_0} \Delta E \, e^{-\frac{\Delta E}{kT}}$$

jer za $\frac{\Delta E}{kT} \gg 1$ je $g_0 e^{\frac{\Delta E}{kT}} \gg g_1$

za $kT \ll \Delta E$ $\quad \lim_{\substack{T \to 0 \\ \beta \to \infty}} S = k \ln g_0 + 0$ $\quad$ jer $\lim_{x \to 0} x \cdot e^{\frac{1}{x}} = \infty$

spec. oblik Boltz. relacije

→ u granici apsolutne nule čestica se mora nalaziti u osnovnom energetskom nivou. g_0 je tada termodin. vjerojatnost

Entropija apsolutne nule

- sistem izgraden od molek. sa magn. momentom
ako je spin $\frac{1}{2}$ onda je $\uparrow\downarrow$ (dvije mogućnosti)
- na sistem djeluje $\vec{H}$

$$U = \vec{H} \cdot \vec{\mu}$$

- magn. moment i spin čestice mogu zauzeti dva antiparalelna položaja

$-H_m \mu$ i $+H_m \mu$

- ako na djeluje $\vec{H}$ onda je broj kvantnih čelija 2.
promatramo sistem kod kojeg ne promatramo oblike kretanja, nego stupnjeve slobode u koje se može postaviti spin

$B = 2^N$ $\quad$ ukupan broj stanja u koja se mogu postaviti čestice N

$$S = k \ln B = Nk \ln 2$$

→ $\vec{H}$ uvijek imamo od samih molekula i pretp. da je T dovoljno niska
$kT \gg \Delta E$ i tada pustimo $T \to 0$ ⇒ sistem teži jednoj od dvije orijentacije i to u stanje niže energije

→ Imamo niz sistema kod kojih je relaksacijsko vrijeme jako veliko τ - ako je vrijeme prelaska molekula jako dugo (u stanje niže energije pri $T \to 0$) - nestabilni sistemi. Imamo dva i više kvantnih stanja koja su istom vjerojatnošću naseljena.

Kristal CO i amorfna tijela imaju drugu vrstu relaksacije i kruto tijelo sadrži primjese koje povećavaju neuređenost i daju doprinos entropiji

ako su konstante kristalne rešetke različite po raznim smjerovima

Negativne temperature

$g(H) \sim e^{-\frac{H}{KT}}$ $\quad \vartheta = KT$ modul kanonske raspodjele mora biti pozitivan ($T>0$) inače integral $\int g(H)d\phi = 1$ divergira

→ kvantizirani energ. spinovi

zanimaju nas stanja max. energije $E_{max} < \infty$

$$W_i = \frac{N_i}{N} = \frac{e^{-1-\alpha} g_i e^{-\beta E_i}}{e^{-1-\alpha} \sum_i g_i e^{-\beta E_i}} \qquad e^{1+\alpha} = \sum_i g_i e^{-\beta E_i}$$

→ $\sum_i$ preko svih stanja da konvergira, mora je i $T<0$

⇒ ako $\exists E_{max}$ ⇒ T može biti i neg. vrijednosti „spekulacija"

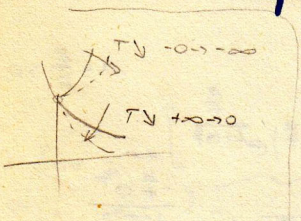
→ rot. & transl. spektri energija ne zadovoljavaju $\exists E_{max}$

pr. energ. spektar je ∞

→ $\exists$ takvi sistemi:

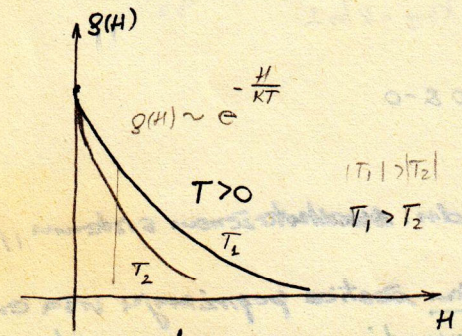
energija dipola μ u $\vec{H}$ $= -\vec{\mu}\vec{H}$ kv. meh. $\exists$ povezanost spina & $\vec{\mu}$

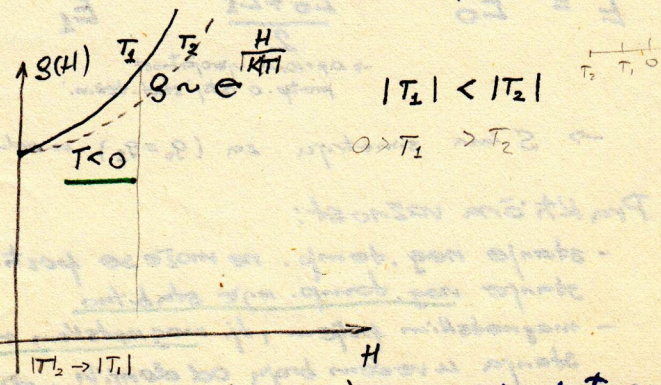
- spin kvantiziran tj. μ u $\vec{H}$ može se postaviti paral. & antiparalelno magn. polju



⇒ moguće energije $-\mu H_m$, $+\mu H_m$ antiparal.

⇒ $\exists E_{max} = +\mu H_m$ i može se govoriti o neg. temp.

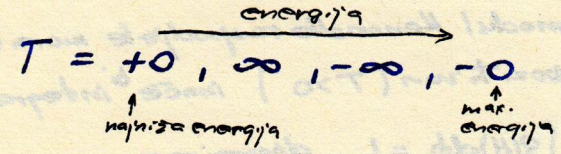


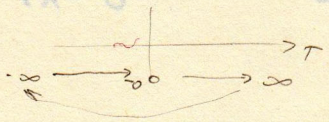


→ za stalnu energiju H, dok $|T| \searrow$ & $T<0$ $(T \to -0)$ ⇒ vjerojatnost popunjavanja viših energ. stanja raste (sve češće nastaje skok. na najviše energ. stanje)

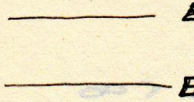
→ ako stavimo u termički kontakt tijelo neg. temp. & pozit. temp.

⇒ prijelaz dopl. sa neg. temp. na poz. temp.





2 nivoa



$g_0 = g_1 = g$ $\quad E_1 - E_0 = \Delta E$

→ vjerojatnost zaposjedanja stanja $\quad W_0 = Ce^{-\frac{E_0}{kT}}$ $\quad W_1 = Ce^{-\frac{E_1}{kT}}$ $\quad W_0 + W_1 = 1 \Rightarrow C$

$$\frac{W_1}{W_0} = e^{-\frac{\Delta E}{kT}}$$

$T = 0 \quad \lim_{T\to 0} \frac{W_1}{W_0} = 0$ ⇒ sve čestice na E_0 osnovnom kvantnom stanju

$T = \pm\infty \quad \lim_{T\to\pm\infty} \frac{W_1}{W_0} = 1$ ⇒ jednaka vjerojatnost nalaženja čestice na E_0 & E_1 ← aprioma vjerojatnost - pretp. o istoj stat. težini

$T = -0 \quad \lim_{T\to -0} \frac{W_1}{W_0} = \infty$ ⇒ sve čestice na E_1 Kvantnom stanju max. energ.

$$S = k\ln\left(g + ge^{-\frac{\Delta E}{kT}}\right) + \frac{g\Delta E}{T\left(ge^{\frac{\Delta E}{kT}} + g\right)} = k\ln g + k\ln\left(1 + e^{-\frac{\Delta E}{kT}}\right)$$

$$\bar{E} = E_0 + \frac{g\Delta E}{ge^{\frac{\Delta E}{kT}} + g}$$

$E_0 + \frac{E_1 - E_0}{2} = \frac{1}{2}$

$a = \frac{E}{k} > 0$

$T = 0$	$T = \pm\infty$	$T = -0$
$S = k\ln g$	$k\ln 2g \to 0$	$k\ln g$
$\bar{E} = E_0$	$\frac{E_0 + E_1}{2}$	E_1

→ aprioma vjerojatnost pretp. o istoj stat. težini

jer $S = k\ln g + k\ln\left[\left(1 + e^{-\frac{a}{T}}\right)e^{\frac{\frac{a}{T}}{1+e^{\frac{a}{T}}}}\right]$

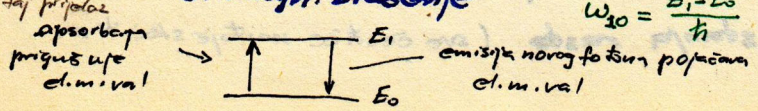
$T \to -0$

$S = k\ln g + k\ln 1$

→ S ima simetriju za $(g_0 = g_1)$ u odnosu na +0 & -0

→ **Praktična važnost:**

- stanje neg. temp. ne može se postići u t-dn. ravnotežnom sistemu, jer stanje neg. temp. nije stabilno
- magnetskim poljem i dj. magnetskom rezonancijom čestice popunjuju više energ. stanja u većem broju od donjih → stanje invertirane raspodjele !



→ prijelazi ovise o populaciji gornjeg i donjeg nivoa

→ sistem s invert. naseljenošću (neg. temp.) ⇒ pojačava el.m.val → **laseri & masери**